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REVISION OF THE ATOMIC WEIGHT OF ALUMINUM.[1]

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Need for a Re-determination of the Atomic Weight of Aluminum.

There is probably no one of the so-called chemical elements equally abundant in nature with aluminum, and occurring in as numerous compounds, with regard to the atomic weight of which our knowledge has long rested upon so slender a foundation of accurate experiment. The following brief statement includes, I believe, all the determinations of this constant which are on record.

Former Determinations.

1. *Experiments of* BERZELIUS, 1812.—Berzelius[2] precipitated a solution of alum by addition of ammonia, dissolved the precipitate in sulphuric acid to saturation, filtered, concentrated the filtrate by evaporation, and threw down aluminum sulphate by alcohol. This salt was well washed with alcohol, to separate as far as possible any excess of acid, and was then heated in a platinum crucible over an alcohol lamp, weighing from time to time, until

[1] From the Philosophical Transactions of 1880. Paper read before the Royal Society, April 22, 1880.

[2] Gilbert's Annalen der Physik, **40** (1812), 260.

no further loss of weight occurred. The anhydrous sulphate so obtained was but slowly soluble in water on heating, but left no insoluble residue. 10 grams of this salt was now raised to a higher temperature in a weighed platinum crucible, and strongly heated as long as any loss of weight could be detected. The residue of loose, light, white alumina found in the crucible weighed 2.9934 grams. Consequently the salt consisted of—

"Sulphuric acid" (SO_3)	70.066 or	100.000
Alumina	29.934 or	42.722
	100.000 or	142.722

Several small arithmetical errors have been made in the discussion of this single experiment of Berzelius, upon which for nearly half a century the value assigned to the atomic weight of aluminum may be said to have rested.

In the original paper it is calculated that if 42.722 parts of alumina contain 19.96 parts of oxygen (the atomic weight of sulphur being then taken =201.16—O=100), 100 parts of alumina must include 46.726 parts of oxygen. This last number should be 46.7207. In a later paper[1] by the same author, it is calculated from the results of the above experiment, that 100 parts of "sulphuric acid" are saturated by 42.7227 parts of alumina, and that the earth contains 46.7047 per cent. of oxygen; the earth is assumed to be Al_2O_3, and consequently the atomic weight of Al is found =171.667 (O=100), or 27.49 (H=1). These numbers, correctly calculated from the percentage of oxygen taken in this second paper, should read 171.167 and 27.39 respectively. Or, if the percentage of oxygen of the former paper, corrected as above, be taken as 46.7207, the atomic weight, for Al_2O_3, will be 171.057 (O=100) or 27.37 (H=1).[2]

Finally, if Berzelius' direct results of experiment be taken, and recalculated with Stas' atomic weights for O (15.96) and S (31.98), the atomic weight of aluminum, its oxide being assumed Al_2O_3, will be 27.237 in reference to that of hydrogen as unity.

Berzelius[3] also attempted to obtain a pure hydrate of aluminum by precipitating the sulphate and nitrate with ammonia, but found

[1] Poggendorff's Annalen der Physik u. Chimie, 8 (1826), 187.

[2] A. C. Oudemans, Jr. (in his Historisch-kritisch Overzigt van de Bepaling der Æquivalent-Gewigten van twee en twintig Metalen; Leiden, 1853), calculates, from Berzelius' figures, Al=171.02.

[3] Gilbert's Annalen, *loc. cit.*

that highly basic salts only were thrown down. Using the chloride instead, a hydrate was obtained which, after being dried in the sun, gave only water on heating, but there was a little loss from mechanically-carried-over alumina. This sun-dried hydrate left 64.932 per cent. of alumina free from acid. Berzelius therefore calculates that 100 parts of anhydrous alumina had been combined with 54 parts of water—this amount of water containing 47.65 parts of oxygen; while the alumina contains, as shown by the above-quoted analysis of the sulphate, 46.726 parts of oxygen. He remarks: "I cannot affirm that either the determination of the amount of water or that of the oxygen in the alumina is sufficiently exact; both are, however, so far so as to sufficiently show us that alumina, like the preceding bases, combines with an amount of water whose oxygen is equal to that of the earth itself."

In the decomposition by heat of aluminum sulphate, as thus used to furnish data from which to calculate the atomic weight of the metal, the following possible sources of error may be noticed: The hydrate precipitated by ammonia from a solution of (presumably) *potash* alum might carry down with it traces of fixed alkali, and this latter be retained in the sulphate afterwards prepared from the hydrate. The tendency of aluminum to form basic salts suggests the possibility of traces of sulphuric acid being lost in the preliminary drying over the simple alcohol lamp, even at a temperature at which possibly the last traces of water might not have been removed. I have found from my own experiments that a trace of basic sulphate may, on the other hand, be obstinately retained even after prolonged exposure to a very high temperature, when it might be assumed that pure alumina alone was left. As Berzelius himself says, ignited alumina rapidly absorbs moisture from the air, involving risk of error in determining its weight. Traces of the light pulverulent alumina are liable to be mechanically carried away during the decomposition of the sulphate. It is observable that all these sources of error, except the last, tend in the same direction, to make the atomic weight of aluminum come out too high.

2. *Experiments of* Sir HUMPHRY DAVY, 1812.—In Sir Humphry Davy's "Elements of Chemical Philosophy"—published in 1812, the same year in which Berzelius' first paper on this subject appeared—it is stated[1] that no direct researches had then been made

[1] Vol. 4, 263, of the Collected Works of Sir H. Davy, edited by his brother Dr. John Davy London, 1840.

on the quantity of oxygen in alumina, but that, from some experiments by the author on the quantity of ammonia required to decompose saturated solutions of alumina in acids, "it would appear that the number representing alumina is about 48, and, supposing it to consist of one proportion of aluminum and one of oxygen, 33 will be the number representing aluminum." The details of the experiments in question are not given, and the combining proportions of all substances having been very imperfectly known at the time—the number 15 is taken above for oxygen—it is needless to say that this passage throws no light upon the exact atomic weight of aluminum.

3. *Experiments of* THOMSON, 1825.—Thomson[1] attempted to deduce the number representing this atomic weight from, (*a*) analyses by himself and others of sundry natural aluminous silicates, (*b*) analyses of potassium alum, and (*c*) analyses of hydrates of aluminum. He concluded from all his experiments that the true number for alumina is 2.25 (O=1), and, taking alumina to be AlO, he made Al=1.25. This corresponds to Al=30, if O be assumed =16, and alumina Al_2O_3—a result which can only be viewed as a rough approximation to the truth, since Thomson's methods were far from accurate, and his experimental results agree but poorly with each other.

4. *Experiments of* MATHER, 1835.—W. W. Mather,[2] Assistant Professor of Chemistry at the United States' Military Academy, West Point, prepared anhydrous aluminum chloride by Wöhler's process, dissolved a weighed portion of it in water, added silver nitrate in excess, filtered off, dried and weighed the silver chloride formed, threw down excess of silver from the filtrate by hydrochloric acid, filtered again, evaporated this second filtrate and washings to dryness, ignited the residue, and weighed it as alumina. .646 gram of aluminum chloride gave 2.0549731[3] grams of silver chloride (yielding on reduction 1.548161 gram of silver) and .2975 gram of alumina.

From the amount of silver chloride found and silver obtained from it in this one experiment, and from the atomic weights of silver and chlorine adopted by Berzelius and Thomson respectively,

[1] Thomas Thomson, M.D., An Attempt to Establish the First Principles of Chemistry by Experiment, **1**, 285; London, 1825.

[2] Silliman's American Journal of Science and Arts, **27** (1835), 241.

[3] The seven decimal places are given, notwithstanding the statement by the author himself that his balance could weigh easily $\frac{1}{3000}$ grain, and was sensible to $\frac{1}{7000}$ grain!

Mather calculated values for the atomic weight of aluminum ranging from 1.82274 to 1.85430 (O=1, and the formula of the chloride being taken as $AlCl_3$), or 29 16384 to 29.66880 for O=16; but from the amount of alumina obtained and the amount of aluminum therein (the latter deduced from the chloride taken for analysis minus the chlorine found), he calculated the atomic weight for aluminum as 1.3188017 (O=1) for alumina taken as Al_2O_3, or 21.1008272 for O=16. He does not seem to have been struck by the evidence of some error in his own work which these discrepant numbers afford, but suggested that the figures given by Berzelius for the aluminum and oxygen in alumina might have been accidentally inverted, which would explain the disagreement between himself and the great Swedish chemist. In reality it is pretty plain that Mather's alumina was not pure, either from fixed matter of some kind left behind from the acids and wash water used, or from absorption of moisture before weighing. If his most direct result only be taken as the basis of calculation, namely, the weight of aluminum chloride used and silver chloride obtained from it, using Stas' numbers for chlorine (35.37) and silver (107.66), the atomic weight of aluminum found will be 28.778 for the formula $AlCl_3$.

5. *Experiments of* MALLET, 1857.—In 1857 the writer of this paper attempted to use metallic aluminum, which had not long before begun to be manufactured and sold, for the determination of the atomic weight. At the meeting of the British Association held in that year at Dublin,[1] he gave a brief account of his experiments, which had been made with the metal of commerce, containing, as he found, only from 93 to 96 per cent. of pure aluminum. The exact nature and amount of the foreign substances present, chiefly iron and silicon, having been determined, the crude metal was dissolved in hydrochloric acid, the solution precipitated by ammonia, and from the amount of alumina left from the precipitate on ignition, after allowing for the impurities, the atomic weight was deduced. The results obtained from a few experiments were not satisfactory enough to warrant any proposal to modify the then received number. The probability that this number needed correction was, however, pointed out, with reasons for such an opinion; the desirability of obtaining for the purpose of new experiments really pure metallic aluminum was noticed; and it was suggested that

[1] Report of British Association Meeting at Dublin, 1857; Transactions of Sections, 53.

difficulties connected with the accurate determination of alumina by the method which had just been tried might make it eligible to determine instead the hydrogen given off during the solution of the metal in acid.

6. *Experiments of* DUMAS, 1858.—Dumas[1] redetermined the atomic weight in question by dissolving in water known weights of aluminum chloride, and ascertaining the quantity of silver, used as nitrate, which was required in each case for precipitation of the chlorine. The aluminum chloride had been carefully prepared on the large scale, then sublimed from iron turnings, and resublimed from aluminum filings. It sometimes still contained traces of iron. Each specimen to be used was sublimed for the last time from aluminum, in a stream of dry hydrogen, into a small glass tube, which was sealed at both ends before the lamp, and reserved for one of the analytical experiments. Of these there were seven. In each the weight of the sealed tube and its contents was taken, a drawn out end opened, and the weight quickly verified after equilibrium of pressure with the outside air had been thus established; the tube was introduced into water, and after solution of its contents the weight of the empty tube was determined. It does not appear from the published paper how the risk of mechanical loss from violent action of the chloride on the water was guarded against; from my own experiments with the bromide this appears to be a point requiring careful attention. Nor is it stated how the quantity of silver used was determined, whether by weighing the chloride of silver formed, by measuring the volume of a standard solution of silver nitrate, or by weighing off a little less metallic silver than would be required, converting this into nitrate, adding it to the aluminum chloride solution, and completing the precipitation with a measured quantity of dilute standard solution of silver nitrate. Nor is it mentioned how, if at all, the error due to slight solubility of silver chloride in the liquid from which it was precipitated is obviated—a point not ignored by Dumas, as appears from another part of the same paper,[2] and afterwards very carefully examined by Stas.

The results of the seven experiments were as follows, the atomic weight or equivalent being calculated for the formula Al_2Cl_3, and on the supposition that Ag=108, and Cl=35.5:—

[1] Annales de Chimie et de Physique [3], **55** (1859), 151. [2] Page 135.

				Atomic Weight.
I.—1.8786	of Al_2Cl_6	required	4.543 of Ag	=13.74
II.—3.021[1]	"	"	7.292 "	=13.85 (should be 13.86)
III.—2.399	"	"	5.802 "	=13.73
IV.—1.922	"	"	4.6525 "	=13.68
V.—1.697	"	"	4.1015 "	=13.77
VI.—4 3165	"	"	10.448 "	=13.68
VII.—6.728	"	"	16.265 "	=13.76
		Mean		13.744
		Should be		13.746 or 27.492 for $AlCl_3$

Recalculating this table for the formula $AlCl_3$, and using the atomic weights of Stas for silver (107.66) and chlorine (35.37), the figures of the last column become—

I.—Atomic weight of Al				. . . .	=27.447
II.	"	"	"	. . . .	=27.696
III.	"	"	"	. . . .	=27.435
IV.	"	"	"	. . . .	=27.318
V.	"	"	"	. . . .	=27.522
VI.	"	"	"	. . . .	=27.327
VII.	"	"	"	. . . .	=27.489
		Mean		. . . . .	27.462

It is to be remarked that the tendency of the chief causes of error connected with these experiments is in the same general direction. The presence of any iron in the chloride used; the action upon it, though but to a minute extent, of any trace of moisture in the hydrogen in which it was finally sublimed; any loss occurring with the fumes formed on introduction of the chloride into water; and the retention of traces of silver chloride in solution in the liquid from which the main mass of this compound had been thrown down; any or all of these would tend to diminish the quantity of silver chloride obtained, and therefore to make the atomic weight of aluminum appear greater than it really is. In discussing results which we owe to the labors of such experimenters as Berzelius and Dumas, it is of course to sources of error likely to inhere in the method itself that attention should especially be given.

Dumas also tried dissolving aluminum (containing iron and silicon in considerable quantity) in hydrochloric acid, adding nitric

[1]Contained traces of iron.

acid in excess, evaporating to dryness, igniting and weighing the alumina (and other oxides) left behind. From an analysis of the crude metal employed, so as to allow for the impurities present, and on the basis of three experiments made as above, he calculated the atomic weight as

13.74 (=27.48 for Al_2O_3—O=16)
13.87 (=27.74 " " — ")
13.89 (=27.78 " " — ")

but he was dissatisfied with these results, having found that the impurities of the metallic aluminum were unequally distributed throughout its mass, and having been unable to obtain the metal in a pure state. He considered the results furnished by the experiments with the chloride as accurate, and concluded that the atomic weight of Al is represented by the number 13.75 (for Al_2Cl_3)—this becomes 27.5 for $AlCl_3$ or Al_2Cl_6.

7. *Experiments of* TISSIER, 1858.—Ch. Tissier[1] prepared aluminum by reducing very pure fluoride of aluminum and sodium —probably cryolite, although this is not stated—by means of purified sodium in a carbon crucible, re-fusing the metal several times in order to free it from any of the flux which might have been retained. No account is given of the means taken to prepare a carbon crucible free from iron and silicon; and to prevent destruction of the crucible by its material burning away during the fusion at high temperature of the aluminum salt with sodium. The metal was tested for iron by dissolving it in nitro-hydrochloric acid, evaporating to dryness with a large excess of nitric acid, and igniting the residue of alumina, which was observed to be of brilliant whiteness, while the addition of a solution containing a few thousandths of iron sufficed "to color it very strongly red." Why the much more delicate tests available for iron in the original solution were not used does not appear.

As regards silicon, it is stated that "the solution of the metal by means of hydrochloric acid left no trace of silicon"; no mention is made of the solution having been evaporated to dryness, the residue remoistened with strong hydrochloric acid and dissolved in water in order to see whether silica was left. A portion of the solution obtained with nitro-hydrochloric acid was evaporated to dryness, the residue ignited, and the alumina so left was digested

[1] Comptes Rendus des Séances de l'Acad. des Sciences, **46** (1858), 1105.

with a strong and boiling solution of ammonium nitrate. This solution was evaporated to dryness, and left a residue of sodium nitrate representing 0.135 per cent. of sodium in the metallic aluminum.

1.935 gram of this aluminum was dissolved in hydrochloric acid, the solution evaporated with an excess of nitric acid until all chlorine was completely driven off, and the residue heated until the nitric acid was also completely removed and alumina only was left. This alumina weighed 3.645 grams. In the paper recording this single experiment the resulting atomic weight is not calculated, but the author simply points out that the number 14, which he says many chemists adopt as representing aluminum, must be too high, while 13.75, the number assigned by Dumas, is in all probability accurate. In support of this view it is calculated that, if Al=14, the alumina obtained in the above described experiment should have weighed 3.590[1] grams; whereas, with Al=13.75, its weight should have been 3.624 grams. In getting these figures O is taken=8.

But, if the minute quantity of sodium stated to have existed in the metal used be deducted, and allowed for as sodium oxide (aluminate) in the last weighed residue, and if the results obtained be calculated, for alumina = Al_2O_3, with Stas' number for oxygen (15.96), the atomic weight of aluminum will be represented by 27.068, a number much nearer to 27 than to 27.5 (13.75×2), the value assumed as most probably correct by Tissier.[2]

8. *Experiments of* TERREIL, 1879.—Lastly, about a year ago Terreil[3] made a determination of the constant in question by passing hydrochloric acid gas over metallic aluminum, collecting and measuring the hydrogen evolved. He placed a known weight of aluminum in a tube of hard glass, the tube wrapped with foil so as to allow of its being made red hot. By one end a stream of well dried gaseous hydrochloric acid could be introduced, while a smaller tube extended from the other end and dipped into a vessel of water.

[1] This ought to read 3.594.

[2] Since this paper was printed in the Philosophical Transactions my attention has been drawn by Prof. F. W. Clarke of Cincinnati to a single other determination made in 1868 by Isnard (Comptes rendus, **66**, 508). The report of this is very brief and without any satisfactory details, the whole of it being the following lines: "The process employed by the author consists in attacking the metal by hydrochloric acid. He finds that 9 grams of aluminum, attacked by pure hydrochloric acid, invariably give, after calcination, 17 grams of alumina; whence he concludes that 9 would represent the equivalent of aluminum as referred to hydrogen taken as unity."

[3] Bulletin de la Société Chimique de Paris, **31** (20 Fév. 1879), 153.

The air was first expelled from the apparatus by a current of dry carbon dioxide, and not until the gas passing through was capable of being completely absorbed by a solution of potash was the hydrochloric acid introduced, this latter itself freed from atmospheric air. The gas escaping from the tube was now collected in a graduated jar, and the temperature of the tube containing the aluminum was raised to a red heat. As soon as hydrogen ceased to come over, the gas in the jar was shaken up with potash to absorb any carbon dioxide which it might contain, and the volume was measured, and reduced by calculation to its equivalent under normal temperature and pressure. The aluminum chloride left in the tube was pulverulent and snow white.

No details are given of the method by which pure metallic aluminum was prepared, although this has been the great difficulty in the way of obtaining accurate results from experiments made with the metal as the starting point, nor is there any record of the tests applied to prove the purity of the metal used. The gas was collected over water, in which hydrogen is not altogether insoluble, and from which more or less of the gases of atmospheric air would be given off into the hydrogen. Nothing is said of the vapor of water, mixed with the hydrogen in proportion depending upon the temperature, having been removed, or its amount calculated and allowed for; though as it is not likely that so obvious a precaution was neglected, it may be supposed that the potash spoken of as used to absorb any carbon dioxide left was either solid hydrate or so strong a solution as to have also removed most if not all the aqueous vapor.

The results of the single experiment reported were:—

Weight of aluminum	.410 gram.
Volume of hydrogen collected at 11° and 768 mm.	530 cc.
Corresponding volume at normal temperature and pressure	508.2 cc.
Weight of this hydrogen	.0455 gram.

from which the author calculates

$$.0455 : .4100 = 1 : 9.01,$$

giving the atomic weight 13.515 (for Al_2Cl_3) or 27.03 (for $AlCl_3$).

In verifying the above calculation I have found as the result of reducing the volume of hydrogen from the given to normal temperature and pressure 514.85 cc. instead of 508.2 cc., but this, I am satisfied, arises from the number representing the pressure at

the time of experiment being, doubtless by a printer's error, wrongly given as 768 instead of 758 mm. With the latter figures the result is as recorded in the paper, and of course such atmospheric pressure is more frequently observed than that which appears in the above table.

It is pretty plain that from the researches which have been quoted we may reject those of Davy, Thomson, and Mather as incapable of giving exact results, this being either admitted by the authors themselves or shown by an examination of their methods and the inconsistency of their conclusions. Our knowledge of the atomic weight under consideration rests therefore upon the investigations of Berzelius, Tissier, and Terreil, each of whom made one experiment, and those of Dumas, who made seven.

General results of former determinations.—If all the results be taken as I have re-calculated them, using Stas' atomic weights for the other elements concerned, and equal value be given to all, we shall have the following arithmetic mean—

Berzelius	27.237
Dumas	27.447
"	27.696
"	27.435
"	27.318
"	27.522
"	27.327
"	27.489
Tissier	27.068
Terreil	27.030
Mean	27.357

If, however, the results of Dumas, all depending on repetition of the same process, be viewed as possibly affected by some constant error, and be thrown together, taking into the calculation the mean only of his seven experiments, the general mean will be—

Berzelius	27.237
Dumas (mean)	27.462
Tissier	27.068
Terreil	27.030
Mean	27.199

If we separate Dumas' results, and take the mean of the other three, we get in contrast—

Berzelius	27.237
Tissier	27.068
Terreil	27.030
Mean	27.112
Dumas (mean)	27.462

Or, if we throw together only the numbers obtained by Tissier and Terreil, which come nearest to each other, we have—

Tissier	27.068
Terreil	27.030
Mean	27.049
Berzelius	27.237
Dumas (mean)	27.462

Values now generally adopted for Atomic Weight of Aluminum.

The number adopted in some of the more recent chemical handbooks, reports, &c., may be quoted as follows:—

GMELIN: Handbook of Chemistry (Cav. Soc. Trans.)	27.4
WATTS: Dictionary of Chemistry, First Supplement	27.4
W. A. MILLER: Elements of Chemistry, 4th edit.	27.5
MEYMOTT TIDY: Handbook of Modern Chemistry	27.5
FRANKLAND: Lecture Notes for Chemical Students	27.5
THORPE: Quantitative Chemical Analysis	27.26
Agenda du Chimiste (WURTZ' Laboratory, 1879)	27.5
Annuaire du Bureau des Longitudes, 1876	27.4
NAQUET: Principes de Chimie, &c., 3e ed.	27.5
FITTICA: Jahresb. üb. d. Fortsch. d. Chemie, 1878	27.4
ROSCOE u. SCHORLEMMER: Ausf. Lehrbuch d. Chemie (Ger. ed.)	27.3
FRESENIUS: Anleit. z. quant. chem. Analyse, 5te Aufl.	27.5
CLASSEN: Grundr. d. anal. Chemie (quant.)	27.3
KOHLRAUSCH: Leitfaden d. prakt. Physik. 2te Aufl.	27.4
MENDELEJEFF: Paper on the "Periodic Law" (transl.)	27.3
J. P. COOKE, Jr.: The New Chemistry	27.5
J. D. DANA: System of Mineralogy, 5th ed.	27.5
E. S. DANA: Text-Book of Mineralogy	27.3

New Experiments by the Author.

During the last three years I have devoted a large part of m leisure time to a re-determination of this atomic weight, sparing no

pains to attain as precise a result as possible, and aiming especially at the discovery, and as far as possible removal, of sources of error connected with the methods employed. The following general principles have been kept in view :—

1. That each process used should be as simple as possible, and should involve as little as possible of known liability to error.

2. That different and independent processes should be resorted to as the means of checking each other's results, even though it may fairly be assumed that one is more advantageous than another.

3. That each process should be carried out with quantities of material differing considerably from each other in successive experiments.

4. That only such other atomic weights should be involved as may be counted among those already known with the nearest approach to accuracy.

The most scrupulous care was taken in the purification and examination of all the reagents used, and as far as possible vessels of platinum or of hard porcelain were substituted for those of glass.

Means and method of weighing employed.—For the weighings an excellent balance, of Becker's construction, was employed. It was in perfect order, carefully adjusted (especially as regards centre of gravity of beam with average load to be carried), and would bear safely 200 grams in each pan, giving when thus loaded a deflection of the index to the extent of 1½ division of the scale over which it moves for a difference of weight of .0001 gram. All weighings were made by the well-known method of observing the vibrations of the index on either side the position of rest. In one series of experiments *absolute* weights were required, *i. e.*, real equality of weight between the quantities of matter dealt with and the standards of weight with which they were compared ; in these cases the method of "double weighing" was made use of, so as to eliminate any error arising from inequality in length of the arms of the balance. In view of this need, in connection with a part of the research, for absolute weights, directly comparable with those used by Regnault in his determination of the density of hydrogen, I applied to my friend J. E. Hilgard, Esq., in charge of the office of the United States' Coast Survey at Washington, for a comparison of a kilogramme with a weight of the same denomination belonging to the Coast Survey, the value of which latter weight is accurately known in terms of the original "kilogramme of the

Archives" at Paris. He kindly had this comparison made, and sent me the results in detail, showing that my weight was 8.1 milligrammes heavier than the "star kilogramme" which is the standard of reference at Washington (both *in vacuo*), with an uncertainty of comparison not exceeding .1 milligramme, while the "star kilogramme" is certified to as agreeing with the normal "kilogramme of the Archives" within 1.1 milligramme. I had already a 10-gramme weight, professedly normal, but, as it turned out, too light by a very minute fraction of its value, and with these two, checked against each other, a full series of comparisons was made of all the other weights to be employed, the specific gravity of each piece being determined before its final comparison as to weight, so that the real values might all be referred to a vacuum by calculation of the buoyancy in air. Determinations of the specific gravity of all materials and vessels which had to be weighed were also made, and, the barometer and thermometer being observed at the time of each weighing, all weights hereafter mentioned in this paper represent real values *in vacuo*.

Three separate series of experiments were made, by methods to be presently stated. A fourth series was attempted, involving the conversion of metallic aluminum into oxide and determination of the amount of oxygen taken up, but this process was found to be attended with much difficulty from various causes, amongst others from the liability to loss by spirting if the metal were treated with acid in open or small vessels, from the necessity of transfer to such vessels for final ignition if larger ones were at first used, and from the appreciable solubility of the hydrate of aluminum if this were precipitated in order to avoid evaporation of the original solution. The few results obtained in this way agreed generally with those of the other methods, but varied among themselves within unsatisfactorily wide limits, and were manifestly not deserving of equal confidence. Hence the work was not pushed further in this direction.

First Series of Experiments.

Purification of ammonium alum.—Ammonium alum of commerce was dissolved in water, a very little nitric acid added, and the liquid boiled in large glass beakers by passing in a current of steam. When the solution had become cold a little ammonium ferrocyanide was added—a very small quantity sufficed to throw down the traces of iron present—and a little animal charcoal,

previously well boiled with strong hydrochloric and nitric acid and thoroughly washed, was stirred in to aid in the subsidence of the minute amount of very finely divided Prussian blue which had been formed. The clear liquid was after about ten days drawn off, and evaporated until the larger part of the alum crystallized out on cooling. The crystals, of which there was obtained more than a kilogramme, were re-dissolved in hot water, and re-crystallized several times (throwing away all the mother liquors), the last time in a porcelain vessel, and with agitation, so as to obtain a granular crystalline powder, which was washed with cold distilled water.

Re-dissolving in water the so far purified alum, now much reduced in quantity, it became necessary to secure the exclusion of the metals of the fixed alkalies, lest their alums should exist in isomorphous admixture with the pure ammonium alum required. To this end aluminum hydrate was thrown down from the solution by addition of ammonia, using not quite enough of the reagent for complete precipitation. The precipitate was well washed with abundance of water, this tedious process being much expedited by the use of a siphon-filter delivering the liquid drawn off into a large flask connected with a powerful aspirator. The bulk of the precipitate was twice re-dissolved in pure hydrochloric acid (each time avoiding complete solution), thrown down again by ammonia, and again washed.

This hydrate was now dissolved in just the necessary amount of dilute and very carefully purified sulphuric acid, and just the proper amount added of ammonium sulphate prepared from the same sulphuric acid neutralized with ammonia. The quantities were determined by bringing the two solutions to known bulks, ascertaining by experiment on a sample of each how much of the respective salts was present, and measuring off the required volumes to be mixed. After concentrating the mixed solution by evaporation it was allowed to crystallize by cooling, and the crystallization was repeated thrice, each time washing with a little cold water. On the last crystallization pains were taken to regulate the rate of cooling so that as far as possible uniformly small crystalline grains were formed of about a millimetre in diameter, thus avoiding the liability of large crystals to contain cavities, in which mother liquor might be retained, and on the other hand securing the possibility of seeing with a lens, better than could have been done if the alum were in a still finer crystalline powder, that all the

crystals as afterwards used were clear and transparent, and showed no signs of efflorescence.

It should be added that all the aqueous ammonia used as above for the precipitation of aluminum hydrate, and for its reconversion into alum, was recently and carefully prepared from ammonium chloride purified from alcoholic amines by boiling with nitric acid as recommended by Stas,[1] that the last crystallizations were effected from water which had been, in pursuance of the practice of the same chemist, distilled from potassium permanganate and hydrate, and that for these last crystallizations a large platinum dish was used, and care was taken that the solution was not allowed to boil, nor even to remain for any length of time near the boiling point, since I ascertained that ammonium alum, like simple ammonium sulphate, gradually gives off small quantities of ammonia on continued boiling of a strong solution. The very last crystallization was carried out with only a sufficient quantity of the alum for a couple of the final experiments.

The salt thus purified was found to be free from any ascertainable content of foreign substances. It gave no trace of coloration in its solution when tested by a ferro-cyanide, tannic acid, &c., and by sulphuretted hydrogen and ammonium sulphide; and spectroscopic examination showed that the fixed alkaline metals and calcium were absent. Silver nitrate gave no indication of chlorine.

Ignition of ammonium alum.—Difficulties connected with this method.—I proposed to ignite a weighed quantity of this alum, whose distinct crystallization gives it the advantage as to definiteness in the amount of water over the simple sulphate used by Berzelius, and to determine the weight of the aluminum oxide left behind, but careful examination of this process showed that two difficulties were to be feared.

In the first place, having rapidly dried the product of the last crystallization by gentle pressure between folds of smooth filtering paper[2] free from loose fibre, portions were weighed off and exposed to the air at about 22° C., with the hope that before long a constant "air-dried" weight would be obtained. It had been previously ascertained that exposure over sulphuric acid led to large loss of water of crystallization within a short time. It was found, however, that even in the air loss of weight went on for so long a time that

[1] Quoted in Fresenius' Zeitschrift fur analyt. Chemie, 6ter Jahrg., 4tes Heft., S. 423.

[2] This had been previously purified by ample washing with acid and water, and well dried.

it could not possibly be referred to mechanically adherent water only. It is true that this loss fell off very rapidly after the first hour or so, but it was impossible to decide precisely when it began to affect the water of crystallization. In order to fully exhibit this I quote the following results obtained from a single large specimen kept very long on hand in a place carefully guarded against dust.

	Grams.
Original weight of alum after one hour's exposure to the air at 22.5° C.	35.7456
Loss of weight in 1st twenty-four hours	.0088
" " 2nd " "	.0025
" " 3rd " "	.0017
" " 4th " "	.0015
" " 5th " "	.0010
" " 6th " "	.0012
" " 7th " "	0009
" " 8th " "	.0011
" " 9th " "	.0007
" " 10th " "	0005

This series of weighings was carried on at longer intervals for six months more; the *monthly* loss was at first .0087 gram, gradually fell off, became as small as .0006 gram in one month of cold weather when the temperature of the room was unusually low, and again rose, with warmer weather, to .0012 gram for the sixth and last month for which the weighings were continued. It was further found that, on placing some of the small crystals of the alum in a glass vessel deep enough to prevent mechanical loss, sensible loss of weight could be produced by the heat developed in simply crushing and pulverizing the salt with a thick square-ended glass rod used as a pestle, and weighed along with the glass and its contents. While, therefore, it might be assumed as probable that mechanically adherent water would be got rid of within a time during which but a very minute quantity of water of crystallization would be lost, a slight doubt is thrown over the exact formula of the salt as analyzed, in reference to this component. Some of the ignition experiments were made with specimens which had been dried by longer exposure to the air than others, as will be noted hereafter.

In the second place it appeared that a minute trace of basic sulphate was retained by the alumina left after ignition at even a very high temperature. This could not be extracted by water, but was detectable by fusion with sodium carbonate free from sulphur,

taking care to use an alcohol flame only. By moistening the alumina with a strong solution of pure ammonium carbonate, re-igniting, and repeating this treatment a second time, it seemed to be possible to remove this source of error, as out of several specimens thus treated only one afforded a barely detectable trace of sulphate.

Details of method adopted.—The actual experiments on the ignition of the alum were carried out as follows. To render uniform the amount of atmospheric condensation on the surface of the vessel weighed, a very light glass bottle was specially made, with a delicately blown stopper, the latter carefully ground in and fitting quite air-tight; the bottle of a size to contain the platinum crucible in which the ignition was to be effected. The crucible was heated to bright redness, and while still quite hot was placed in a desiccator at some distance above a surface of recently distilled sulphuric acid. When cooled down to the temperature of the balance-room the crucible was as quickly as possible transferred to the weighing bottle, which was at once closed, and the combined weight of bottle and crucible was taken. The stopper was then removed for an instant, the cover of the crucible raised, and the quantity of alum desired, which had been roughly weighed off in a tube, having been poured in, occupying in no instance more than one-third

Fig. 1.

depth of the vessel, cover and stopper were replaced, and a second weighing gave, by the gain upon the first, the exact amount of alum used. Attached to the inner side of the crucible cover was a piece of rather stout platinum wire, which, when the cover was in place, ran down into the crucible in the line of its axis of figure,

carrying two little diaphragms of platinum foil perforated with small holes (see fig. 1); such a diaphragm having been suggested and used by Dumas[1] in his researches on atomic weights as the means of preventing any loss of solid particles which might otherwise be carried off mechanically from the substance ignited. To avoid inconvenience from the fusion of the alum in its water of crystallization, and the swelling up of the salt to a bulky, porous mass, the heating was conducted very gradually. The platinum crucible was kept for an hour at 90° C., then for an hour at 100°, for an hour at 110°, another hour at 120°, a like time at 140°, and was then gradually brought to ignition over an argand alcohol lamp. It was then placed inside a larger platinum crucible, resting on a flat bit of unglazed porcelain at the bottom of the latter, and exposed to a gradually increased, and at last bright yellow heat in a gas furnace of Fletcher's construction. This temperature was maintained for a full hour. On cooling down, the smaller crucible was taken out, the cover cautiously raised, and enough of a strong solution of ammonium carbonate introduced to moisten the alumina. Drying gently in a steam-bath, the crucible was reignited over an alcohol blast lamp, producing a strong red heat, and the addition of ammonium carbonate, drying, and ignition once repeated. As soon now as the crucible had ceased to be visibly red hot it was placed in the desiccator as at first, allowed to cool down to the temperature of the balance-room, quickly transferred to the weighing bottle, the stopper of which was inserted, and the final weighing was made while the alumina in the crucible was thus protected from absorption of moisture from the air. These experiments were carried out during a period of remarkably steady weather, with very little variation of atmospheric temperature, pressure, or moisture in the balance-room during the whole series.

Direct results of first series of experiments.—The results were as follows:

A.—Alum dried by exposure to air for 2 hours at 21°–25° C.

I.—8.2144	grams of	$(NH_4)_2(Al_2(SO_4)_4.24H_2O$	left	.9258	gram of Al_2O_3.
II.—14.0378	"	"	"	1.5825	"
III.— 5.6201	"	"	"	.6337	"
IV.—11.2227	"	"	"	1.2657	"
V.—10.8435	"	"	"	1.2216	"

[1] Annales de Chimie et de Physique, *loc. cit.*

B.—Alum dried by exposure to air for 24 hours at 19°–26° C.

VI.—	12.1023	grams of	$(NH_4)_2Al_2(SO_4)_4.24H_2O$	left 1.3660	gram of Al_2O_3.
VII.—	10.4544	"	"	1.1796	"
VIII.—	6.7962	"	"	.7670	"
IX.—	8.5601	"	"	.9654	"
X.—	4.8992	"	"	.5528	"

(*To be continued.*)

NEW PHENETOL DERIVATIVES.

By Edward J. Hallock.

Para-bromo-ortho-nitro-phenetol is readily prepared from phenetol, by first acting upon it in the cold with pure bromine, and then treating the well washed product with strong nitric acid. The bromo-nitro compound thus obtained is at first a thick oily liquid, which solidifies on standing to a yellow mass of crystals. By recrystallization from alcohol colorless needles were obtained, which melt at 47° C. The compound has an agreeable aromatic odor. This method of preparation is simple, and yields satisfactory results. By reduction with tin and hydrochloric acid it yields, according to Stebbins, a para-bromo-ortho-amido-phenetol.

An attempt was made to prepare the ortho-bromo-para-nitro-phenetol by the action of bromine upon an alcoholic solution of paranitro-phenetol, obtained from phenetol as described in this Journal, **1**, 271. The reaction does not take place smoothly, and the product obtained is not pure. When little or no heat is employed, the resultant compound fuses at 54°, a point suspiciously near the melting point of para-nitrophenetol, viz. 58°. The quantity obtained was not sufficient for an analysis. At a higher temperature an entirely different compound was obtained, which melted at about 138° C. The percentage of bromine indicated a mono-bromo-nitro-phenetol. It was contaminated by a small quantity of a yellow dye-stuff slightly soluble in hot water, and possessed of remarkable tinctorial power. The very high melting point of this ortho-bromo-para-nitro-phenetol is somewhat exceptional, and when perfectly pure may be found to differ somewhat

from that above stated. Damm and Staedel[1] state that monobromo-para-nitro-anisol melts at 106°.

Ortho-chloro-para-nitro-phenetol is very readily prepared from para-nitro-phenetol by acting on it with potassic chlorate and hydrochloric acid. It forms a yellow oil, solidifying at once to a mass of crystals, which melt, when purified by recrystallization, at 77°. The para-chloro-ortho-nitro-phenetol, as stated in an earlier paper, this Journal, **2**, 258, melts at 61°, a difference of 16° only.

Phenetol is much more easily attacked, it will be seen, by the halogens, chlorine and bromine, than by nitric acid, but in every case the reagent which is first made to act on it forms a para substitution product, while the second substitution takes place in the ortho position; and takes place, generally, with far greater ease than when the para position had not yet been occupied. Does the capture of a para bond weaken that of the ortho carbon atom and render it more defenseless than before?

The following table of melting or boiling points for the phenetol derivatives thus far known will serve to show how the isomeric compounds differ from one another in this respect:

Name of Compound.	Characteristic.	Authority
Para-chloro-phenetol	boils 233°,	Lippmann[2]
Ortho-chloro "	" 208°,	Beilstein[3]
Para-chloro "	" 210°, melts 21°	"
Ortho-nitro "	" 258°,	Groll[4]
Para-nitro "	melts 58°,	Fritzsche[5]
o-Chloro-p-nitro-phenetol	" 77°,	Author
p-Chloro-o-nitro "	" 61°,	Faust[6]
o-Bromo-p-nitro "	" 138°,	Author
p-Bromo-o-nitro "	" 47°,	"

Ortho-bromo-phenetol has not yet been described so far as I can ascertain.

[1]Berl. Ber. **13**, 838; Jahreb. rein. ch. **7**, 311. [2]Wien. Acad. Ber. **62**, 611.
[3]Berl. Ber. **7**, 1395. [4]J. pr. Chem. [2], **12**, 207.
[5]Ann. Chem. Pharm. **110**, 155. [6]Zeitschr. f. Chem. [2], **5**, 1869, 450.

Southern Medical College, Atlanta, Ga., *Jan.*, 1881.

PRELIMINARY NOTICE OF A NEW VEGETABLE COLORING MATTER.

By Sam. P. Sadtler and Wm. L. Rowland.

Some months since our attention was drawn to a variety of wood, called *Beth-a-barra*, which had been recently imported from the west coast of Africa, and was much valued for its extreme toughness and its capability of receiving a high polish.

The wood is compact, very heavy, and in color very nearly resembles ordinary black walnut. On close examination, however, the interstices of the fibres are plainly seen to be filled with a yellow crystalline powder. In this respect it differs from logwood, barwood, camwood and red sandal wood, with which it was compared. In these woods the color is uniformly disseminated, the fibre appearing as if soaked in a solution of corresponding color. It resembles more closely the yellow coloring matter of rhubarb and of araroba, or goa-powder, which compound, chrysophanic acid, occurs also as a loose yellow crystalline powder in the interstices of the root. Special attention was, therefore, paid to its resemblances to this compound, as well as to those of the well-known dye-woods mentioned above.

A cross-section of the Beth-a-barra wood appears very similar to the fernambouc and sappan woods, from which brasilin is obtained.[1] It bears very little resemblance, however, to the sections of logwood and the other therein-mentioned woods.[2]

The coloring principle was extracted from the shavings, or better yet, the sawdust and raspings of the wood, by heating with distilled water containing a little sodium carbonate. This produced a deep claret-red solution, which was then filtered. To the filtrate acetic acid was added in slight excess, precipitating the coloring matter in a fine flocculent condition; this was filtered, washed and then dissolved in hot 80 per cent. alcohol, from which it crystallized upon cooling. By successive crystallizations the pure substance was obtained.

The material thus gotten was a tasteless, yellow compound apparently crystallizing in scales or needles. Upon examination under the microscope these plates are found to be made up of a

[1] Amer. Journ. Pharm. p. 348, 1880. [2] loc. cit. p. 351.

series of flat prisms, joined laterally. The crystals are unchanged in dry or moist air, insoluble in cold water, very slightly soluble in hot water, but readily soluble in alcohol or ether. The presence of even a trace of alkali or alkaline carbonate also causes it to dissolve with deep claret-red color. The crystals melt at 135°C.

Two lots were prepared for analysis; one was dried at 100°C., and the other at 125°C.

Analysis of material dried at 100° C.

	I.	II.	Mean.
Carbon, . .	68.75	68.79	68.77
Hydrogen, . .	6.05	6.05	6.05
Oxygen, . .	25.20	25.16	25.18
	100.00	100.00	100.00

Analysis of material dried at 125° C.

	I.	II.	Mean.
Carbon, . .	75.82	75.00	75.41
Hydrogen, . .	6.39	6.69	6.54
Oxygen, . .	17.79	18.31	18.05
	100.00	100.00	100.00

The mean of the results of the analysis of that dried at 125°C. would give a formula $C_{28}H_{29}O_5$, or possibly $C_{22}H_{23}O_4$, while that dried at 100°C. would be $C_{28}H_{29}O_5 + 3H_2O$.

The accepted formula for hæmatoxylin, the coloring material of logwood, is $C_{16}H_{14}O_6$[1], which would give 63.57 per cent. of carbon and 4.63 per cent. of hydrogen.

Taking the work done within the past few years on hæmatoxylin as a guide, the action of numerous reagents was then tried upon the new coloring matter. We will give for comparison the results arrived at with hæmatoxylin and then state our results with the Beth-a-barra color.

Sodium amalgam has no action upon hæmatoxylin; with this coloring matter, however, we obtained, on treatment with sodium amalgam, a white compound, which under the microscope is seen to be crystallized in fine needles. The examination of this we reserve for a future communication.

[1] Ber. deutsch. chem. Gesell. **4**, 329.

A drop of nitric acid added to the ethereal solution of hæmatoxylin in the cold rapidly oxidizes it; nitric acid oxidizes this coloring principle only when concentrated, and with the aid of heat, giving rise to a white crystalline compound, soluble in ether, which gradually decomposes on exposure to the air.

Hæmatoxylin, when fused with potassium hydrate, yields pyrogallic acid; this material, on fusion with potassium hydrate, yields no pyrogallic acid.

When hæmatoxylin is treated with ammonia solution and is allowed to stand in contact with the air for several days, an oxidation product is obtained[1]; the Beth-a-barra principle, treated in this manner for several days, shows no signs of any oxidation or change.

Reagents.	Brasilin.	Hæmatoxylin.	Santalin.	Beth-a-barra.
Alkalies,	Claret-red sol.	Reddish-purple sol.	Claret-red sol.	Claret-red sol.
Acids—weak,	Orange ppt.	Pink solution,	Light red ppt.	Yellow ppt.
Acids—conc.,	Yellow solution,	" "	Dark red sol.	Yellow sol.
Alum sol.,	Crimson-red ppt.	Yellow solution passing into violet.	Santalin thrown out.	Coloring matter thrown out, does not combine with Al_2O_3
Lime water,	Crimson ppt.	Bluish-purple ppt.	Reddish-brown ppt.	Acts like alkalies.
Ferrous salts,	Purplish-black ppt.	Bluish-black ppt.	Reddish-violet ppt.	Fine reddish chocolate ppt.
Ferric salts,	Brownish-red ppt.	Black ppt.	Reddish-brown ppt.	Chocolate brown ppt.
Copper salts,	Brownish-red ppt.	Purple sol.	Red ppt.	Brown changing to yellow ppt.
Lead salts,	Crimson-red ppt.	Violet sol.	Reddish-violet ppt.	Brick red precipitate.
Mercuric salts,	Yellow ppt.	Yellow sol.	Scarlet ppt.	Orange yellow ppt.
Silver salts,	Yellow ppt.	Gray ppt.	Reddish-brown ppt.	Deep red ppt.
Tartar emetic,	Rose-colored ppt.	Purple sol.	Cherry-colored ppt.	Orange ppt.
Stannous chloride,	Red ppt.	Purple ppt.	Red ppt.	Yellow ppt.
Sodium Aluminate.	Claret-red ppt.	Purple ppt.	" "	Claret-red ppt

It is a noteworthy fact that though this substance contains more hydrogen relatively than brasilin or hæmatoxylin, it does not oxi-

[1] Handwörterbuch d. Chemie, 3, 542.

dize as readily, but is reduced more readily than either of these coloring compounds. The above table has been prepared, comparing the action of a series of reagents upon several of the common coloring principles with the results obtained with this coloring material. The brasilin and santalin were extracted directly from the woods with alcohol, and the other two were alcoholic solutions of the crystallized coloring matters.

The following references, all of them to papers in the Berichte der deutschen chemischen Gesellschaft, show what has been done with the investigation of these vegetable coloring matters in late years: Franz Reim—"Ueber das Hæmatoxylin," 4, p. 329; Adolf Bæyer —"Ueber das Gallein," 4, p. 457; E. Kopp—"Ueber Brasilin und Resorcin," 6, p. 446; C. Liebermann and O. Burg—"Ueber Brasilin," 9, p. 1883; Richard Meyer—"Verhalten des Hæmatoxylins bei der trockenen Destillation," 12, p. 1392; E. A. Letts—"Ueber das Phtalein des Hæmatoxylins," 12, p. 1651.

A comparison of the Beth-a-barra coloring material with chrysophanic acid, the yellow coloring principle of rhubarb and goa powder, was then made in order to see what resemblance there might exist between the two.

Chrysophanic acid forms golden-yellow scales, melts at 162°C., forms deep red-colored solutions with caustic alkalies or ammonia, from which the acid is precipitated in yellow flakes on neutralizing the solution with acid. Caustic soda will extract the color from solutions of chrysophanic acid in ether, chloroform, benzol, or petroleum benzin, yielding deep red solutions; ammonia will extract the color from solutions in ether or petroleum benzin, but not from chloroform or benzol solution, An ammoniacal solution is precipitated lilac by acetate of lead and rose-colored by alum.

The Beth-a-barra color looks like chyrsophanic acid, but fuses at 135°C.; forms solutions with alkalies like those of chrysophanic acid. Caustic soda and ammonia both will extract the color from solutions in ether, benzol, petroleum benzin and chloroform. An ammoniacal solution is precipitated brick-red by acetate of lead, and no compound apparently is formed in alum solutions. Chrysophanic acid, when ignited with zinc dust, yields methyl-anthracene; this compound similarly treated yields phenol-like bodies with the odor of wood-tar creosote, and soluble in alkali with violet color. Finally, the percentage composition of this compound, before quoted, differs too decidedly from that of chrysophanic acid, which requires 70.87 per cent. carbon and 3.94 per cent. hydrogen.

Nor does the Beth-a-barra principle correspond exactly with chrysarobin, which Liebermann and Seidler found[1] to be the chief constituent of goa powder. That compound dissolves in strong potassium hydrate solution with yellow color and green fluorescence. Its percentage composition moreover demands 72.29 per cent. of carbon and 5.22 per cent. of hydrogen. By heating with caustic potash solution in contact with air it is changed into chrysophanic acid.

The similarity of the Beth-a-barra principle in many of its reactions to these two compounds leads one to suspect a relationship. We hope to be able to settle what this relationship is shortly by a fuller study of its reactions and derivatives.

PHILADELPHIA, *Dec.* 21, 1880

CONCERNING PHTHALIMIDE.

BY M. KUHARA,
Fellow in Chemistry, Johns Hopkins University

In a paper on the oxidation of orthotoluenesulphamide[2] it has been shown by Remsen and Fahlberg that, when orthosulphobenzoic acid is treated with phosphorus pentachloride and ammonia, it is converted into benzoic sulphinide, $C_6H_4\left\{\begin{matrix}CO\\SO_2\end{matrix}\right\}NH$. It is probable that the normal chloride of the acid is first formed, and that when this is treated with ammonia, the ammonium salt of sulphaminebenzoic acid is formed, which when treated with hydrochloric acid yields the sulphinide:

$$C_6H_4\left\{\begin{matrix}SO_2Cl\\COCl\end{matrix}\right\}+4NH_3+H_2O=C_6H_4\left\{\begin{matrix}SO_2NH_2\\COONH_4\end{matrix}\right\}+2NH_4Cl, \quad \text{and}$$

$$C_6H_4\left\{\begin{matrix}SO_2NH_2\\COONH_4\end{matrix}\right\}+HCl=C_6H_4\left\{\begin{matrix}SO_2\\CO\end{matrix}\right\}NH+H_2O+NH_4Cl.$$

It seemed probable from a consideration of these reactions that phthalic acid when treated in a similar way would yield phthalimide, and, at the suggestion of Professor Remsen, I have made some experiments in the direction indicated.

[1] Ber. d. deutsch. chem. Ges. **11**, 1603. [2] This Journal, **1**, 426.

Phthalyl chloride was made according to the directions of Ador,[1] by boiling phthalic acid (1 mol.) with phosphorus pentachloride (2 mol.) and a little oxychloride. On treating this with aqueous ammonia it passed into solution, and now on adding hydrochloric acid a bulky precipitate was produced. This dissolved easily by heating; on cooling, a mixture of white scaly crystals with a minute quantity of fine needles was deposited, while on still further concentrating the mother liquor phthalic acid crystallized out. By recrystallizing the mixture from alcohol, beautiful transparent rhombohedral crystals were obtained, and from the mother-liquors the needle-shaped crystals mentioned above were deposited. The rhombohedral crystals, which were obtained in larger quantity than the needles, were analyzed:

I. 0.2 gram gave 14.74 cc. N after corrections.

II. 0.196 gram gave 14.78 cc. N after corrections.

A substance of the formula $C_6H_4\left\{\begin{matrix}CO\\CO\end{matrix}\right\}NH$, that is of the formula of phthalimide, requires 9.52 per cent. N, while the quantities found correspond to 9.21 and 9.42 per cent. respectively.

The substance is, however, quite distinct from phthalimide. It is soluble in cold alcohol and water, more readily in boiling alcohol and water, while phthalimide is not soluble in cold alcohol and water. It melts without decomposition when heated, and sublimes in flakes. It dissolves in concentrated sulphuric acid and water, throwing down phthalic anhydride from the solution. It melts at 192°, the imide at 230°. It gives no precipitate with silver nitrate.

From the knowledge thus far gained it seems as though this substance must be regarded as an isomeride of phthalimide. According to von Gerichten[2] it appears probable that phthalyl chloride is either $C_6H_4\left\{\begin{matrix}CCl_2\\CO\end{matrix}\right\}O$, or a mixture of this substance with the normal chloride. If this view is correct, the formation of a substance isomeric with phthalimide might easily be accounted for. The action of ammonia upon a substance of the formula $C_6H_4\left\{\begin{matrix}CCl_2\\CO\end{matrix}\right\}O$ might give rise to a product of the formula $C_6H_4\left\{\begin{matrix}C(NH)\\CO\end{matrix}\right\}O$, which would be isomeric with phthalimide. The formation of such a substance would be exceedingly interesting and its study attractive. I regret to say that though I made re-

[1] Annalen der Chemie, **164**, 230. [2] Berichte d. deutsch. chem. Gesell. **13**, 417

peated efforts to get possession of more of this product, they all failed, and I was obliged to give up its study. It is strange that in the first experiment just exactly the right conditions for its formation should have been found, and that these could not again be met with.

In the subsequent experiments it was found that when phthalyl chloride is treated with ammonia and hydrochloric acid, phthalic anhydride is precipitated. It was also shown that when ammonium phthalamate is treated with hydrochloric acid, phthalic anhydride is precipitated. When phthalyl chloride is dissolved in ammonia and the solution concentrated to a very small volume, phthalamic acid, $C_6H_4\begin{cases}COOH\\CONH_2\end{cases}$, is deposited. This was carefully compared with phthalamic acid prepared from phthalic anhydride, according to Marignac's directions,[1] and the two were found to be identical.

The connection known to exist between phthalic anhydride, phthalamic acid, phthalimide and phthalyl chloride, would then lead to the conclusion that all these bodies have a similar structure. Phthalamic acid is made from ammonium phthalate by heating, and the only equation which will represent this reaction satisfactorily is the one commonly used:

$$C_6H_4\begin{cases}COONH_4\\COONH_4\end{cases}-NH_3-H_2O=C_6H_4\begin{cases}CONH_2\\COOH.\end{cases}$$

Further, when phthalamic acid is heated it gives off water and is converted into phthalimide:

$$C_6H_4\begin{cases}CONH_2\\COOH\end{cases}-H_2O=C_6H_4\left\{\begin{matrix}CO\\CO\end{matrix}\right\}NH.$$

It is possible, of course, to conceive of the formation of the isomeric substance, $C_6H_4\left\{\begin{matrix}C(NH)\\CO\end{matrix}\right\}O$, under these circumstances, but its formation does not appear probable. While then it is impossible to decide positively what the formula of phthalimide is, the probabilities are in favor of the one commonly accepted.

Now, when phthalyl chloride is treated with gaseous ammonia it is converted directly into phthalimide. The reaction takes place very easily, and is accompanied by a decided evolution of heat. The substance possessed all the properties of phthalimide as described by Laurent and Marignac. The yield was excellent;

[1] Annalen der Chemie, **42**, 219.

apparently almost quantitative. Assuming that phthalimide has the commonly accepted formula, the only way to represent this transformation of the chloride satisfactorily is by the equation:

$$C_6H_4\begin{Bmatrix}COCl\\COCl\end{Bmatrix}+3NH_3=C_6H_4\begin{Bmatrix}CO\\CO\end{Bmatrix}NH+2NH_4Cl.$$

But this leads to the view that the chloride has the normal structure, whereas, as was stated above, the experiments of von Gerichten indicate that the chloride is $C_6H_4\begin{Bmatrix}CCl_2\\CO\end{Bmatrix}O$. It is possible that a substance isomeric with phthalimide is formed when phthalyl chloride is treated with ammonia, and that this is then converted spontaneously into the imide.

A few derivatives of phthalamic acid were made, as this substance has been but very imperfectly studied. The only salts of the acid which have hitherto been prepared are those of silver and ammonium. In order to prepare the imide it was found most convenient to pass dry ammonia into a flask containing phthalic anhydride, slightly heated. A violent reaction took place, the mass instantly melting, and then soon solidifying again. The solid mass was essentially pure imide.

To an aqueous solution of phthalimide there was added an excess of baryta water and the two boiled together. A current of carbon dioxide was then passed through the cooled solution, the precipitated barium carbonate filtered off, and the clear filtrate concentrated. The salt does not crystallize from an aqueous solution, the latter finally becoming syrupy in consistency and remaining so even after long standing. If alcohol be added to the concentrated aqueous solution the salt is thrown down as a white, amorphous powder, being entirely insoluble in alcohol. This was filtered off, dried and analyzed:

0.1135 gram precipitated barium salt gave 0.057 gram $BaSO_4$.

Calculated for $\left(C_6H_4\begin{Bmatrix}CONH_2\\CO_2\end{Bmatrix}\right)_2Ba$	. .	29.46 per cent. Ba.
Found	. .	29.47 " "

Potassium phthalamate, $C_6H_4\begin{Bmatrix}CONH_2\\COOK.\end{Bmatrix}$ This salt was prepared by the gradual addition of a very dilute solution of potassium sulphate to the solution of the barium sulphate. After

filtering off the precipitated barium sulphate, the solution was left to evaporate slowly over sulphuric acid. After several days, very fine, silky, transparent needles crystallized out. It is easily soluble in alcohol and water. It gives off ammonia when boiled with potassium hydroxide, and hydrochloric acid throws down phthalic anhydride from its solution.

Copper phthalamate was prepared from the barium salt by precipitating with a solution of copper sulphate. It does not crystallize, but gradually separates in the form of an amorphous powder.

Phthalamic is an exceedingly weak acid and its salts are not well characterized compounds.[1]

Contributions from the Chemical Laboratory of Harvard College.

IX.—RESEARCHES ON THE SUBSTITUTED BENZYL COMPOUNDS.

By C. Loring Jackson.

SUBSTITUTED BENZALDEHYDES.[2]

By J. Fleming White.

The ortho- and parachlorbenzaldehydes are the only compounds of this class containing a single halogen atom which have been described heretofore. The former, made by Henry[3] from salicylal-

[1] The fusing point of phthalic acid has been the subject of considerable discussion, the last statement bearing upon it having come from E. Ador (Annalen der Chemie, **164,** 239). Ador says that crystallized phthalic acid melts at 213° and the powder of the same substance at 203°. The discrepancies in the statements on record seem to be due to the fact that when the acid is heated, it is partly converted into its anhydride before its fusing point is reached. The presence of the anhydride tends to lower the fusing point, and this is the lower the more anhydride there is formed. If the acid is heated slowly, or if it be used in the form of powder, more anhydride is formed and the fusing point is lower. Some special experiments were made with the pure acid to test the correctness of this view. Small quantities were heated in U-tubes placed in paraffin baths at the temperatures of 140° and 170°. In both cases anhydride was formed and the fusing point of the acid considerably lowered. Under exceptional conditions the fusing point of pure phthalic acid may be observed as high as 213°, but usually it will be found to vary considerably. To test the purity of the acid, it is advisable to make the anhydride and then crystallize this, when pure, from water.—I. R.

[2] Presented to the American Academy. Communicated by the Authors.

[3] Ber. d. ch. G. **2,** 135.

dehyde by treating it with an excess of phosphoric pentachloride and decomposing the orthochlorbenzalchloride ($C_6H_4ClCHCl_2$) formed with water in a sealed tube at 170°, was a heavy colorless oil boiling between 210° and 220° and oxidized even by the air into orthochlorbenzoic acid.

The so-called parachlorbenzaldehyde was first made by Beilstein and Kuhlberg[1] by boiling chlorbenzylchloride, $C_6H_4ClCH_2Cl$, with plumbic nitrate and water, according to the method of Lauth and Grimaux[2]; also by heating chlorbenzalchloride, $C_6H_4ClCHCl_2$, with water in a sealed tube at 170°, and by treating benzaldehyde with chlorine in presence of iodine. Later, Berlin[3] obtained it by distilling trichlorbenzylamine, $(C_6H_4ClCH_2)_3N$, with bromine and water, and Sintenis by the action of chlorine on chlorbenzylethylether, $C_6H_4ClCH_2OC_2H_5$. They all describe it as a heavy oil, and Berlin gives its boiling-point as 210°–220°.

As the chlorine compounds used by Beilstein and Kuhlberg, Berlin and Sintenis[4] were all made by the action of chlorine on toluol in the cold, and must therefore have contained the corresponding ortho-compounds,[5] a revision of their work is necessary.

Parachlorbenzaldehyde, C_6H_4ClCOH, was made by boiling 10 grams of parachlorbenzylbromide, melting-point 48°, with 14 grams of plumbic nitrate and 100 grams of water for three days in a flask with a return-cooler, which was kept full of carbonic dioxide during the boiling and subsequent distillations to prevent oxidation of the aldehyde by the air. The aldehyde, separated by distillation from the plumbic bromide formed, solidified in the cooler in long white needles, which were purified by solution in acid sodic sulphite and filtering; the filtrate concentrated by evaporation deposited on cooling crystals of the double salt of the aldehyde and acid sulphite, which were washed twice with cold alcohol, dried, dissolved in a small quantity of hot water, and decomposed by distillation with solid sodic carbonate. The pure aldehyde, thus obtained, was dried over sulphuric acid in an atmosphere of carbonic dioxide and analyzed.

0.2112 gram gave on combustion 0.4613 gram CO_2 and 0.0680 gram H_2O.

	Calculated for C_7H_5ClO.	Found.
Carbon	59.78	59.56
Hydrogen	3.56	3.57

[1]Ann. Chem. Pharm. **147**, 352. [2]Ibid. **143**, 80. [3]Ibid. **151**, 140.
[4]Ber. d. ch. G. **4**, 697. [5]This Journal, **2**, 85.

Properties. Long white needles melting at 47°, which sublime very easily; slightly soluble in water, very soluble in alcohol, ether, benzol, carbonic disulphide, and glacial acetic acid. Potassic permanganate oxidizes it rapidly, air slowly, converting it into parachlorbenzoic acid.

The following substituted aldehydes were prepared from the corresponding bromides by the same method. In solubility they all resemble the parachlorbenzaldehyde.

Parabrombenzaldehyde, C_6H_4BrCOH.

0.5000 gram of the substance gave on combustion 0.8268 gram CO_2 and 0.1298 gram H_2O.

	Calculated for C_7H_5BrO.	Found.
Carbon	45.40	45.10
Hydrogen	2.70	2.88

Long white needles melting at 57°. With oxidizing agents or air it forms parabrombenzoic acid.

Paraiodbenzaldehyde, C_6H_4ICOH.

0.7339 gram of substance gave on combustion 0.9665 gram CO_2. The hydrogen was unfortunately lost.

	Calculated for C_7H_5IO.	Found.
Carbon	36.20	35.90

White needles melting at 73°. With oxidizing agents it forms paraiodbenzoic acid.

Metabrombenzaldehyde, C_6H_4BrCOH.

0.5900 gram of substance gave on combustion 0.9800 gram CO_2 and 0.1320 gram H_2O.

	Calculated for C_7H_5BrO.	Found.
Carbon	45.40	45.30
Hydrogen	2.70	2.49

A colorless heavy oil, showing no signs of solidifying even in a freezing mixture of ice and salt. With oxidizing agents, or on exposure to the air, gives very easily metabrombenzoic acid.

Orthobrombenzaldehyde, C_6H_4BrCOH, was prepared from the liquid orthobrombenzylbromide, as this work was done before it

had been obtained in the solid state. Instead of distilling the product of the reaction, the plumbic bromide and water were decanted while hot, leaving the aldehyde as a heavy oil, which was washed with water, purified as before described with acid sodic sulphite, dried, and analyzed.

0.5440 gram of substance gave, on combustion, 0.8990 gram CO_2 and 0.1476 gram H_2O.

	Calculated for C_7H_5BrO.	Found.
Carbon	45.40	45.08
Hydrogen	2.70	3.01

A heavy colorless oil, much more rapidly oxidized by the air than any of the other substances described in this paper.

The three para-compounds yielded, when treated in alcoholic solution with sulphuretted hydrogen, the thioaldehyde, as a reddish white varnish, which it did not seem worth while to investigate.

X.—ON FURFUROL AND CERTAIN OF ITS DERIVATIVES.[1]

By Henry B. Hill.

In December, 1876, by the kind invitation of Dr. E. R. Squibb, I had the opportunity to examine the working of a new process for the manufacture of acetic acid by the dry distillation of wood at a low and carefully regulated temperature, as it was carried on under his direction at Brooklyn, N. Y. I then noticed that, in the rectification of the crude wood spirit, a yellowish oil passed over with the vapor of water after the more volatile portions had been distilled off. Its high specific gravity and its peculiar odor made me anxious to examine it more closely.

A short study of it was sufficient to show that it contained large quantities of furfurol, which could be isolated in a pure state with little trouble, and I therefore undertook at once the study of the constitution of furfurol and pyromucic acid. Before my investigations were far advanced, Baeyer[2] published the first of his papers upon the constitution of furfurol, in consequence of which my own

[1] Proceedings Amer. Acad. of Arts and Sciences. Communicated by the Author.

[2] Berichte der deutsch. chem. Gesellsch. **10**, 355.

work was naturally discontinued. At the same time, however, I wrote to Professor Baeyer asking if I could not make use of the large supply of material which I had at hand without interfering with the plan of his research. In reply I received the extremely considerate intimation that a study of mucobromic acid and its derivatives would in no way interfere with his work.

This investigation was begun in 1877; and, although it is not yet completed, so many facts have accumulated that I have thought it best to publish an account of the results already obtained.

Different portions of this research I have carried on with Mr. O. R. Jackson and Mr. C. F. Mabery, assistants in this laboratory, and with Mr. W. Z. Bennett. In my description of our results I shall make plain the share which each of these gentlemen has had in the work.

My most sincere thanks are due to Dr. Squibb for the generous supply of material, without which it would have been impossible for me to have undertaken this investigation.

Furfurol one of the Products of the Dry Distillation of Wood.

Although the products formed in the dry distillation of wood have repeatedly been made the subject of investigation, I can find in the literature of the subject but little reference to the presence of furfurol among them. That furfurol is thus formed is asserted by Gmelin[1] on the authority of Völkel, but a close examination of Völkel's original papers[2] fails to show any sufficient foundation for the assertion. Although Völkel had already shown that furfurol was formed in the dry distillation of sugar, and had established its presence by analysis[3], in his subsequent work upon the dry distillation of wood he seems to have based his conclusions solely upon qualitative tests by no means conclusive. Although he makes a number of general statements concerning the presence of furfurol among the products he obtained, I can find nothing more definite than is contained in the following passage[4]:

After describing the extraction of a yellowish brown oil from the pyroligneous acid by means of ether, he proceeds: "In Kalilauge löst sich das Oel unter Entwicklung eines betäubenden Geruchs auf, der von einer geringen Menge einer organischen Basis herrührt,

[1]Gmelin's Handbuch, **7**, 599; Suppl. **2**, 972.
[2]Poggendorff's Annalen, **82**, 496; **83**, 272 and 557; Ann. Chem. u. Pharm. **86**, 66.
[3]Ann. Chem. u. Pharm. **85**, 59.
[4]Ibid. **86**, 83.

weil er auf Zusatz von Säure wieder verschwindet. Die dunkel gefärbte alkalische Lösung trübt sich in kurzer Zeit durch Ausscheiden eines gelbbraunen Körpers, der Pyroxanthin enthält. Aus der abfiltrirten noch stark gefärbten alkalischen Flüssigkeit wird durch verdünnte Schwefelsäure ein anderer brauner Körper abgeschieden, und zugleich der Geruch des Kreosots wahrgenommen. Aus diesen Reactionen ergiebt sich dass das Oel . . . ein sehr gemengtes . . . ist. Es enthält ein eigenthümliches Oel (Pyroxanthogen), das durch die Einwirkung von Alkalien in Pyroxanthin übergeht; Kreosot; ferner mehrere flüchtige Oele, die durch Alkalien in braune Körper umgeändert werden die in Kali theils löslich theils unlöslich sind. Diese letzteren Oele sind unstreitig identisch mit den flüchtigeren Oelen die bei der Destillation des Zuckers erhalten werden, Furfurol, u. s. w." I have quoted the passage with but little abbreviation, that the character of the qualitative tests upon which Völkel based his conclusion may be appreciated.

Quite recently since the publication of a preliminary note by me upon this subject, V. Meyer[1] has found in the commercial glacial acetic acid of the continent, a small quantity of furfurol which manifested itself by the intense red color developed when the acid was mixed with aniline.

Although these two observations are all I can find recorded of the presence of furfurol among the products of the dry distillation of wood, its formation from wood by other means has been more frequently noticed. Although Döberciner[2] could obtain no furfurol from sawdust by distillation with sulphuric acid, Fownes[3] none from linen, and Cahours[4] and Gudkow[5] were equally unsuccessful with pure cellulose, Emmet[6] obtained it by the same method from woody fibre, Stenhouse[7] from sawdust, afterward from mahogany[8] and madder.[9] Gr. Williams[10] also found that it was formed when wood was heated under pressure with water, although none could be obtained at ordinary pressures. Similar results were obtained by H. Müller.[11]

A brief description of the method of distillation which has furnished the material for this investigation may prove of interest:

[1]Berichte der deutsch. chem. Gesellsch. **11,** 1870. [2]Journ. prakt. Chem. **46,** 168.
[3]Pharmaceutical Journal and Transactions, **8,** 113. [4]Ann. Chim. Phys. [3] **24,** 277.
[5]Zeitschr. für Chem. 1870, 360. [6]Am. Jour. **32,** 140.
[7]Ann. Chem. u. Pharm. **35,** 301. [8]Ibid. **74,** 278.
[9]Ibid. **80,** 325. [10]Chem. News, **26,** 231 and 293. [11]Ibid. **26,** 247.

since the product obtained in this way contains considerable quantities of furfurol, while the percentage formed by the ordinary methods must be very small to have escaped notice so generally. The wood, chiefly oak, is cut into small pieces and filled into rectangular retorts of boiler iron, each one capable of holding a charge of from five to six thousand kilogrammes. The retorts when charged are placed in separate cells of an oven heated by hot-air flues. The temperature of this oven is carefully regulated by means of long mercurial thermometers built into each cell, and the thermometer readings vary from 150° at the beginning of a distillation to 200° at the end. The average time required is six days, and during this time the wood loses about thirty-two per cent. of its weight. The volatile products pass through an outlet pipe at the top of each retort, and are condensed in a set of ordinary coolers.

The wood left in the retorts after distillation is darker in color and somewhat more brittle than the fresh wood: its composition agrees essentially with that given by Payen[1] for dried oak wood. The specimens of wood for analysis were taken while still warm from the retorts, and kept hermetically sealed until analyzed.

I. 0.4480 gram substance gave 0.8950 gram CO_2, 0.2545 gram H_2O and 0.0040 gram ash.

II. 0.3880 gram substance gave 0.7810 gram CO_2 and 0.2220 gram H_2O. 1.2725 gram of the same wood gave 0.0070 gram ash.

III. 0.3270 gram substance gave 0.6390 gram CO_2, 0.1740 gram H_2O and 0.0015 gram ash.

	Found.			Payen.
	I.	II.	III.	
C	50.01	54.89	53.30	54.44
H	5.88	6.29	5.78	6.24
Ash	0.89	0.55	0.46	

The volatile products of the distillation are subjected to the ordinary processes of rectification. In fractioning the wood spirit, after the more volatile portions have passed over, the distillate throws down a heavy yellow oil upon dilution with water, and somewhat later the slightly acid aqueous distillate contains an abundance of the same heavy oil in suspension. The quantity of oil which thus separates in the course of distillation amounts to between three and four tenths of one per cent. of the crude wood spirit taken, although I am unable to form even an approximate estimate of what proportion this may be of the total amount present.

[1] N. Ann. Sci, Nat. **11**, 24.

The oil, as I received it, was feebly acid to test paper, and had a peculiar aromatic odor. It was bright yellow in color, and slightly heavier than water. It was washed with water, dried over calcic chloride and submitted to fractional distillation. The liquid began to boil a little above 100°, but the thermometer rose rapidly and had reached 160° before any considerable quantity had passed over; between 160–170° it remained stationary for a long time, and then rose again rapidly to over 200°. After several distillations, about sixty per cent. of the oil taken distilled between 160° and 165°, the greater part of which boiled steadily at 162°. The boiling point and general character of the oil at once suggested the presence of furfurol, and this was readily proved by its conversion into furfuramide, furfurine, and pyromucic acid. The behavior of the oil to alkalies, however, showed that it was still by no means homogeneous. When shaken with a dilute solution of potassic or sodic hydrate, a brilliant yellow color was developed; and in a few moments the clear liquid became turbid with the separation of a flocculent yellow precipitate, which proved to be chiefly pyroxanthin. In following out the method of purification which was thus suggested I found it most convenient to separate from the crude oil only so much of the higher boiling constituents as could be removed by rejecting that which passed over above 175° in two successive distillations. The distillate collected below 175° was then gradually mixed with one-fourth its volume of a concentrated solution of sodic hydrate, taking care to keep the mixture cool, and shaking the two well together. After standing a short time the oil was separated from the alkaline solution, washed with a little water, and distilled with steam. The furfurol thus obtained was sufficiently pure for all ordinary purposes, and from such a product was made all the pyromucic acid which has been used in the course of the following investigations.

For its conversion into pyromucic acid it was mixed with an equal volume of a concentrated alcoholic solution of sodic hydrate, and carefully stirred until the violent reaction was over. The sodium salt was then thoroughly washed with ether, dissolved in hot water, and decomposed by concentrated hydrochloric acid. For the purification of the crude acid it was dissolved in a cold dilute solution of sodic carbonate, taking care that the solution should remain slightly acid. The filtered solution of the sodium salt was boiled with bone-black, filtered, concentrated by evaporation, and

finally acidified with hydrochloric acid. The acid which separated on cooling was then recrystallized from boiling water, and was found on analysis to be sufficiently pure for further use.

0.8140 gram substance gave 1.5910 gram CO_2 and 0.2910 gram H_2O.

	Calculated for $C_5H_4O_3$.	Found.
C	53.57	53.31
H	3.57	3.97

The acid prepared in this way melted at 128–129°; and, since the melting point of pyromucic acid is usually given somewhat higher, it seemed advisable to subject this product to further purification. Mr. J. J. Thomsen, therefore, prepared the ethyl-ether of the acid by saturating its solution in absolute alcohol with hydrochloric acid, precipitating with water, and washing first with a dilute solution of sodic carbonate and then with water. He then found that the carefully dried ether distilled from the first drop to the last unchanged at 195° (mercury column completely in vapor) under a pressure of 766 mm. On cooling, it crystallized in large transparent prisms, which melted at 34°. According to Malaguti[1], ethyl pyromucate melts at 34°, but boils at 208–210°, under a pressure of 756 mm. For the determination of boiling point we employed about 30 grams of the ether, and an analysis showed its purity.

0.5615 gram of substance gave 1.2330 gram CO_2 and 0.2940 gram H_2O.

	Calculated for $C_5H_3O_3C_2H_5$.	Found.
C	60.00	59.87
H	5.71	5.81

A portion of this ether was saponified with sodic hydrate, the acid liberated from the sodic salt, recrystallized from hot water several times, and finally melted. The solidified acid melted at 130.5° (uncor.), while an acid made directly from mucic acid melted at 130°. The corrected melting points of the two were 133° and 132.5°; whereas Schwanert[2] gives the corrected melting points 134.3° and 132.6° respectively for substance made from furfurol and from mucic acid. The chief constituent of the oil under investigation was thus shown to be furfurol. From the higher boiling portions I have as yet been able to isolate no well-marked substances. On distillation, the thermometer rose slowly to over 300°, and even after long fractioning there appeared to be no tendency towards

[1]Ann. Chim. Phys. [2] **64**, 279. [2]Ann. Chem. u. Pharm. **116**, 257.

constant boiling points. By far the greater portion was insoluble in alkalies, and I could obtain no characteristic derivatives by the action of various reagents.

From the sodic hydrate used for washing the crude furfurol could be separated in small quantity an oil volatile with steam, and possessing a strong odor like smoked fish. It had the general characters of a phenol, but I have not as yet further identified it. Since a large quantity of material has been accumulated in preparing the furfurol necessary for the following researches, I hope before long to make further study of the less volatile constituents which are present in smaller quantity.

Mucobromic Acid.

Mucobromic acid was first made by Schmelz and Beilstein[1], in 1865, by the action of bromine and water upon pyromucic acid. They found its salts so unstable that they made little attempt to isolate them, but confined themselves chiefly to the study of the decomposition which ensued when it was boiled with alkalies, and of the reaction effected by argentic oxide.

They found that the acid was rapidly decomposed when boiled with baric hydrate, that bromacetylen was set free, and that baric carbonate was precipitated. In solution, they found, beside baric bromide, a sparingly soluble barium salt, to which they gave the name baric muconate, and the formula $BaC_4O_3.H_2O$. This formula was, however, based upon a single barium and two water determinations. They also prepared the free muconic acid, but made no further study of it than to establish the fact that it was a crystalline solid readily soluble in water, and that its lead salt was insoluble. They expressed the reaction which they supposed had taken place by the equation:

$$2C_4H_2Br_2O_3+H_2O=C_4H_2O_3+C_2HBr+2CO_2+3HBr.$$

They also found that mucobromic acid was attacked when boiled with argentic oxide and water, that argentic bromide was formed, and at the same time a silver salt quite insoluble in water. This silver salt, according to their calculations of the analytical results which they obtained, had the formula $C_5H_2Br_2Ag_2O_5$, and they regarded this as an intermediate product standing between mucobromic and muconic acids. The acid was found to be a crystalline

[1] Ann. Chem. u. Pharm. Suppl. 3, 276.

solid, which appeared to give bromacetylen and muconic acid when heated with baric hydrate. The reaction with argentic oxide they wrote:

$$2C_4H_3Br_3O_3 + 2Ag_2O = C_7H_2Br_3Ag_3O_5 + AgBr + H_2O + CO_2.$$

In the course of the investigations upon mucic acid and its derivatives, which were begun in Limpricht's[1] laboratory in 1868, mucobromic acid received more or less attention. Although it was found to be the only product when pyromucic acid was treated with water and an excess of bromine at ordinary pressures, Limpricht and Delbrück showed that it was completely decomposed when heated in a sealed tube to 120° with bromine and water, provided that three molecules of bromine, at least, were used to one of mucobromic acid. As products of the decomposition, they found, beside carbonic dioxide and hydrobromic acid, tribromethylenbromide, C_2HBr_5, perbromathylenbromide, C_2Br_6, tetrabrombutyric (?) acid, $C_4H_4Br_4O_2$, and dibromfumaric (?) acid, $C_4H_2Br_2O_4$. The marks of interrogation appear in Limpricht's original paper. Limpricht and Lessing also found in one experiment that, by the reduction of mucobromic acid, a liquid was formed which boiled at about 120° and contained 84.8 per cent. of carbon, 8.8 of hydrogen, and the remaining 6.4 per cent. was oxygen. They were, however, unable to repeat the experiment with a like result.

In attempting the preparation of mucobromic acid, Mr. O. R. Jackson and I found that we were unable to obtain a satisfactory yield by following the method given by Schmelz and Beilstein or by Limpricht. Schmelz and Beilstein say that the quantity of water taken is not a matter of indifference, but neither they nor Limpricht make any specific statements as to the amount which they found to be most advantageous. They agree, however, that the bromine should be added slowly as long as it is taken up in the cold, that the solution should then be heated and bromine added as long as the color continues to disappear.

According to this method we were unable to get more than 25 per cent. of the theoretical yield; and at the same time we were obliged to use quite a large excess over the amount of bromine calculated from the equation:

$$C_5H_4O_3 + 4Br_2 + 2H_2O = C_4H_3Br_3O_3 + CO_2 + 6HBr.$$

[1] Berichte d. deutsch. chem. Gesellsch. **2**, 211; **3**, 90, 671; **4**, 805; Zeitschr. für Chem. 1869, 599; Ann. Chem. u. Pharm. **165**, 253.

We soon found that our yield was greatly increased and the excess of bromine proportionately decreased if the bromine was added rapidly. Later, when it was found that a low temperature was essential to the formation of mucochloric acid, the pyromucic acid and water were cooled with ice until the bromine had all been added, but the yield was not perceptibly affected.

We have obtained the best results by the following method: Pyromucic acid is suspended in ten times its weight of water contained in a flask fitted with reverse cooler and drop-funnel. The calculated amount of bromine is then rapidly added, cooling only so far as may be necessary to avoid loss of bromine. After the bromine is all added, the flask is heated, and the liquid kept boiling for ten or fifteen minutes. The solution may then be allowed to crystallize direct, although we have usually evaporated it until the hydrobromic acid began to volatilize in abundance before allowing it to cool. In either case the crystals should be well washed with cold water and recrystallized from boiling water. In this way we have found it easy to obtain 70 per cent. and over of the theoretical yield.[1]

The acid recovered from the mother liquors is usually very dark colored, and it cannot be purified by recrystallization from water either with or without the addition of bone-black. We have found, however, that such an acid may be obtained perfectly white by one or two recrystallizations from dilute sulphuric acid (1 : 4).

As to the properties of mucobromic acid, we can only confirm the statements of Schmelz and Beilstein. It crystallizes ordinarily from water in irregular leafy aggregates, from acid solutions or from certain other solvents in distinct rhombic plates. From a solution in concentrated hydrobromic acid we have frequently obtained it in large compact crystals, with edges 10 to 12 mm. in length, but so striated as to render measurement impossible. It is sparingly soluble in cold water, very readily in hot water, in alcohol or in ether. In benzol or carbonic disulphide it is very sparingly soluble in the cold, but dissolves quite readily on heating. Chloroform takes up a little when hot, most of which it deposits on cooling. In warm concentrated sulphuric acid it dissolves freely, and, if not too strongly heated, crystallizes out on cooling or on dilution. It melts at 120–121°, and at a higher temperature it distils in part unchanged.

[1]Under conditions favorable to complete crystallization from the concentrated hydrobromic acid which forms the mother liquors, we have obtained 78 per cent.

The following analyses may serve to show the purity of the material used in the course of the following investigations:—

I. 0.7840 gram substance gave 0.5390 gram CO_2 and 0.0720 gram H_2O.

II. 0.9326 gram substance gave 0.6340 gram CO_2 and 0.0712 gram H_2O.

III. 0.2347 gram substance gave 0.3421 gram AgBr.[1]

IV. 0.2331 gram substance gave 0.3410 gram AgBr.

Calculated for $C_4H_2Br_2O_3$.		Found.			
		I.	II.	III.	IV.
C	18.60	18.75	18.55		
H	0.77	1.02	0.85		
Br	62.02			62.03	62.25

Salts of Mucobromic Acid.

Schmelz and Beilstein found that mucobromic acid decomposed baric carbonate, and that the barium salt thus formed was readily soluble in water, although it was decomposed during the spontaneous evaporation of the solution. As it seemed a matter of some interest to determine whether mucobromic acid was capable of forming salts, Mr. O. R. Jackson and I pursued the investigation one step further.

Baric Mucobromate, $Ba(C_4HBr_2O_3)_2$. We found that an aqueous solution of mucobromic acid dissolved baric carbonate readily, that the solution on standing soon turned brown, deposited a brownish flocculent precipitate, and contained then a baric bromide in abundance. On heating, the same change took place more rapidly, and when the solution was boiled a substance was volatilized with the steam which had a sharp, acrolein-like odor, and reduced silver oxide on heating. Although this change was rapid near 100°, we found that it was sufficiently slow at 50–60° to allow the preparation of a solution saturated at this temperature, which on cooling with vigorous stirring deposited crystals of the barium salt. The mucobromic acid was suspended in very little water, the whole warmed to 50–60°, baric carbonate added in excess, and the solution filtered and cooled as rapidly as possible. Even with these precautions we found it difficult to saturate the acid completely without bringing about decided decomposition. The salt, therefore,

[1] All the determinations of halogens in this and the subsequent investigations were made according to the method of Carius.

usually contained more or less free acid, from which it could be completely freed by washing with ether. The salt when dried *in vacuo* over sulphuric acid hardly lost weight at 100°, but when heated a few degrees higher it turned brown and gave out the sharp, penetrating odor mentioned above. Analyses I. and II. were made with a preparation crystallized from water without subsequent washing, III., IV., and V. with substance washed with ether.

I. 0.9479 gram gave 0.5018 gram CO_2 and 0.0547 gram H_2O.

II. 0.3434 gram gave, on ignition with H_2SO_4, 0.1165 gram $BaSO_4$.

III. 0.4186 gram gave, on ignition, 0.1482 gram $BaSO_4$.

IV. 0.5747 gram gave, on ignition, 0.2030 gram $BaSO_4$.

V. 0.7638 gram gave, on ignition, 0.2695 gram $BaSO_4$.

Calculated for $Ba(C_4HBr_2O_2)_2$.		Found.				
	I.	II.	III.	IV.	V.	
C	14.74	14.44				
H	0.30	0.63				
Ba	21.04		19.95	20.82	20.77	20.74

This salt is readily soluble even in cold water, and soluble also in alcohol. On boiling its aqueous solution, the decomposition described above ensues, with the evolution of carbonic dioxide. This reaction has not yet been farther studied.

Argentic Mucobromate, $AgC_4HBr_2O_3$. The silver salt may be made by adding a concentrated solution of argentic nitrate to a solution of the barium salt. Since it is quite soluble even in cold water, it is better to use, instead of the barium, the calcium salt, in order to facilitate washing. It is precipitated in fine, felted needles, which blacken quite rapidly on exposure to diffused light, and are decomposed at once on moistening with alcohol or warming with water; argentic bromide is formed, together with some metallic silver. This substance was dried *in vacuo* for analysis:—

I. 0.3601 gram gave 0.1862 gram AgBr.

II. 0.5640 gram gave 0.2903 gram AgBr.

Calculated for $AgC_4HBr_2O_3$.		Found.	
		I.	II.
Ag	29.59	29.70	29.56

Ethyl Mucobromate. The ethyl ether of mucobromic acid may readily be made by saturating its solution in absolute alcohol with hydrochloric acid, or more conveniently by warming this solution

with concentrated sulphuric acid. If considerable sulphuric acid be used, the ether often crystallizes out on standing in large well-formed crystals, otherwise it is precipitated by the addition of water and washed with a dilute solution of sodic carbonate. The crude product contains impurities which can be removed only by repeated recrystallization from alcohol. This recrystallization is more conveniently accomplished if the moderately saturated solution is cooled to 0°. The ether crystallizes in large, transparent forms of the monoclinic system, which melt at 50–51° and boil at 255–260° with partial decomposition. When slightly warmed it has a pungent, aromatic odor.

The analysis of substance dried *in vacuo* over sulphuric acid gave:

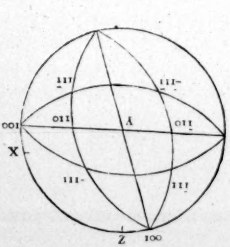
I. 0.8583 gram substance gave 0.7933 gram CO_2 and 0.1686 gram H_2O.

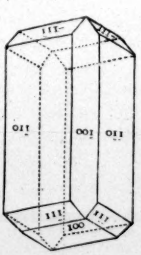
II. 0.7000 gram substance gave 0.6432 gram CO_2 and 0.1377 gram H_2O.

Calculated for $C_4HBr_2O_3,C_2H_5$.		Found. I.	II.
C	25.17	25.24	25.05
H	2.10	2.18	2.18

Mr. Mabery has studied the crystalline form of this substance, and obtained the following results:—

CRYSTALLINE FORM OF ETHYL MUCOBROMATE.





Monoclinic System. — Forms observed, — $\{\bar{1}11\}\{111\}\{100\}\{001\}\{110\}$.

$$a : b : c = 1.053 : 1 : 1.221 ; \quad ac = 78° 27'.$$

Angles between Normals.—

	Found.	Calculated.
111 : 1$\bar{1}$1	82° 11′	
110 : 1$\bar{1}$0	92° 7′	Fundamental angles.
111 : 1$\bar{1}$0	32° 56′	
111 : 001	64° 53′	64° 46′
111 : −1$\bar{1}$1	72° 11′	71° 50′
001 : −1$\bar{1}$1	52° 44′	52° 53′
1$\bar{1}$0 : −1$\bar{1}$1	29° 8′	29° 17′
110 : 1$\bar{1}$0	87° 50′	87° 53′
110 : 001	81° 50′	82° 1′
1$\bar{1}$0 : 001	98° 4′	97° 59′
110 : 1$\bar{0}$0[1]	45° 37′	46° 4′

Action of Phosphoric Pentabromide and Acetylchloride.

Mr. O. R. Jackson studied with me the behavior of mucobromic acid towards phosphoric pentabromide and acetylchloride.

Mucobromylbromide. When mucobromic acid is mixed with about four times its weight of phosphoric pentabromide, and the mixture heated for a short time at 110–115°, a quiet reaction sets in, the mass becomes liquid, and water then precipitates a heavy red oil, which after thorough washing with water gradually solidifies at ordinary temperatures, or immediately if cooled to 0°. This substance is very soluble in alcohol, ether, benzol, chloroform, or carbonic disulphide, but crystallizes well from a solution in a little hot alcohol when this is cooled to 0°. After repeated crystallization from alcohol, it forms small, slender prisms, which melt at 55–56°, and have the percentage composition corresponding to mucobromylbromide.

I. 0.6643 gram substance gave 0.3755 gram CO_2 and 0.0374 gram H_2O.

II. 0.2598 gram substance gave 0.4573 gram AgBr.

III. 0.2252 gram substance gave 0.3964 gram AgBr.

	Calculated for $C_4HBr_3O_2$.	Found. I.	Found. II.	Found. III.
C	14.96	15.41		
H	0.31	0.63		
Br	74.77		74.89	74.89

The behavior of this substance towards alkalies is especially

[1] The form { 1$\bar{0}$0 } was observed upon two or three individuals only, and the reflections were imperfect.

characteristic. The reaction may best be observed when baric hydrate is cautiously added to a dilute alcoholic solution. An intense indigo-blue color is at once developed, which, however, soon passes through green to reddish yellow, with the simultaneous formation of a brown-red, flocculent precipitate. The same brown precipitate is formed when the mucobromylbromide is boiled in an excess of baric hydrate; but the two products which are most characteristic of the decomposition of mucobromic acid under the same conditions, bromacetylen and malonic acid, are formed in such small quantities that they may easily be overlooked. This peculiar behavior led us to suppose at first we had not the simple bromanhydride of mucobromic acid in our hands, but that an hydroxyl group outside the carboxyl had been replaced. A more careful study showed, however, that such was not the case. Although this mucobromylbromide is apparently little affected even by hot water, on boiling it is gradually decomposed, and the solution then contains mucobromic acid (m. pt. 120–121°). Absolute alcohol decomposes it with more difficulty; still, after several hours' boiling with reverse cooler, on evaporating the excess of alcohol and cooling strongly, crystals separated which had the characteristic form of the ethylmucobromate, and which melted at 51° after recrystallization from alcohol.

Mucobromic Acetanhydride. When mucobromic acid is heated in a sealed tube for several hours with an excess of acetyl chloride at 120°, or when it is heated under ordinary pressure with acetic anhydride, a substance is formed which is very soluble in alcohol, ether, or chloroform, and which may be purified by precipitation by water from its alcoholic solution. It falls as a colorless oil, which gradually solidifies in slender, dendritic needles, which melt at 53–54°.

0.9015 gram gave 0.8050 gram CO_2 and 0.1290 gram H_2O.

	Calculated for $C_4HBr_2O_3.C_2H_3O$.	Found.
C	24.00	24.36
H	1.33	1.59

That the acetyl group enters the carboxyl in this case is shown by the behavior of ethyl mucobromate to acetyl chloride. After several hours' heating, with an excess of acetyl chloride, at 140–150°, the ether was found to be unaltered. The substance which was obtained crystallized in the form of the ethyl-ether, melted at 50°,

and upon analysis proved to contain the required percentage of bromine.

0.2720 gram gave 0.3600 gram AgBr.

Calculated for $C_4HBr_3O_3.C_2H_5$.		Found.
Br	55.94	56.32

Action of Bromine.

Limpricht and Delbrück studied in detail the action of bromine and water upon mucobromic acid, but they made no experiments with dry bromine. It therefore seemed advisable to investigate the action of dry bromine; since the reactions in this case would naturally be less complicated than with aqueous bromine, and on that account might prove to be of more service in determining the constitution of mucobromic acid. In my first experiments I employed equal molecules of bromine and mucobromic acid, but soon found that one molecule of bromine sufficed for the complete decomposition of nearly two molecules of mucobromic acid, although the products of the reaction were essentially the same whether the bromine was used in excess or not.

At 100° very little action was noticeable; at 120–130° the action was marked, but so slow that the temperature was raised to 140°. Here the reaction ran rapidly, and after two hours the bromine had disappeared. On cooling, the tubes were filled with long, prismatic crystals, which were permeated with a nearly colorless oil. On opening the tubes, hydrobromic acid gas escaped in abundance, and with it could be detected a comparatively small amount of carbonic dioxide. The partially solidified product of the reaction was treated with small quantities of cold water. The greater part of the prismatic crystals were in this way carried into solution; while the oil, in which a small quantity of crystals were yet to be seen, was left undissolved. This aqueous solution, upon evaporation, left a white, crystalline acid, very soluble in water, which for purification was converted into the barium salt. Before neutralizing the aqueous solution with baric carbonate, I found it best to evaporate to dryness, and take up a second time with a little cold water, in order to remove the small quantity of undecomposed mucobromic acid which often was present. The barium salt was precipitated several times from aqueous solution by alcohol, and finally crystallized from water by evaporation. Thus purified, it formed brilliant, transparent, rhombic plates, which lost water in desiccator slowly, but which I

was unable to dehydrate perfectly by heat, either at ordinary pressures or *in vacuo*, without causing partial decomposition. The analysis of the air-dried salt gave percentages required by a barium salt of dibrommaleic acid containing two molecules of water of crystallization.

I. 0.8687 gram of substance lost, at 120°, 0.0624 gram H_2O. Of this dried salt, 0.4145 gram gave, by ignition, 0.2341 gram $BaSO_4$.

II. 0.5780 gram of air-dried salt gave, by ignition, 0.3010 $BaSO_4$.

Calculated for $BaC_4Br_2O_4.2H_2O$.		Found.	
		I.	II.
Ba	30.78	30.86	30.63
H_2O	8.09	7.07	

This salt is hardly more soluble in boiling water than in cold; in dilute alcohol, it is almost insoluble. The solubility in water was determined according to the method of V. Meyer.

I. 7.1377 gram of a solution saturated at 19° gave, on evaporation with H_2SO_4 and ignition, 0.2296 gram $BaSO_4$.

II. 6.9649 gram of a solution saturated at 19° gave 0.2249 gram $BaSO_4$.

An aqueous solution saturated at 19°, therefore, contains of the anhydrous salt the percentages:

I.	II.
5.65	5.67

The silver salt could best be made by the precipitation of a solution of the free acid by argentic nitrate. From dilute solution it separated in long, flat needles; from concentrated solutions it was precipitated in small prisms. It proved to be almost insoluble even in hot water. The dry salt exploded violently on heating, or by percussion.

0.6311 gram of the salt, dissolved in dilute nitric acid, gave 0.4859 gram AgBr.

Calculated for $Ag_2C_4Br_2O_4$.		Found.
Ag	44.27	44.22

The lead salt fell as a crystalline precipitate upon the addition of plumbic acetate even to a dilute solution of the free acid.

The acid was liberated from the pure barium salt by the addition of normal sulphuric acid, in quantity insufficient for complete precipitation; the aqueous solution was allowed to evaporate spontane-

ously ; and the acid was then separated from the excess of barium salt by means of ether free from alcohol. Prepared in this way, the acid formed a mass of indistinct, aggregated needles, extremely soluble in water, ether, or alcohol ; and almost insoluble in boiling chloroform, benzol, ligroin, or carbonic disulphide. From a mixture of ether and chloroform it could be crystallized in the form of fine, felted needles.

After standing in desiccator, the acid gave on analysis too high a percentage of bromine (I). It was therefore washed with chloroform, the excess of chloroform evaporated in a paraffine desiccator according to Liebermann's suggestion ; but the percentage of bromine remained essentially unaltered (II). I therefore dissolved the acid in hot water, allowed the solution to evaporate spontaneously, and dried by exposure to the air alone, but failed to alter its composition (III). Subsequently I dissolved the pure anhydride described below in hot water, and found that the acid obtained by spontaneous evaporation of this solution when air-dried also contained more bromine than the formula of the acid required (IV).

I. 0.2050 gram substance gave 0.2860 gram AgBr.
II. 0.2305 gram substance gave 0.3200 gram AgBr.
III. 0.2150 gram substance gave 0.3000 gram AgBr.
IV. 0.2500 gram substance gave 0.3475 gram AgBr.

Calculated for $C_4H_2Br_2O_4$.		Found.			
		I.	II.	III.	IV.
Br	58.38	59.37	59.08	59.38	59.15

From these experiments it would appear that the acid, even at ordinary temperatures, is partially converted into its anhydride. This change goes on rapidly at temperatures near 100°, so that it is impossible to obtain constant melting points. The preparations analyzed melted at 120–125° when warmed with ordinary rapidity. The acid was but slightly volatile with steam, but could be distilled with greatest readiness with the vapor of concentrated hydrobromic acid.

From this acid the anhydride could be obtained without difficulty in a pure state, by heating to 120° in a current of dry carbonic dioxide. The sublimation began at 100°, or possibly lower, but became rapid at 115–120°. The anhydride condensed in lustrous, flattened needles, which melted at 114–115°. In cold water it dissolved but slowly ; in alcohol, ether, benzol, ligroin, chloroform, or carbonic disulphide, it was readily soluble.

I. 0.3672 gram gave 0.2510 gram CO_2 and 0.0010 gram H_2O.
II. 0.2630 gram gave 0.3870 gram AgBr.

Calculated for $C_4Br_2O_3$.		Found. I.	II.
C	18.75	18.65	
H	—	0.02	
Br	62.50		62.61

The aqueous solution obtained by treating the original product from the action of bromine with cold water, therefore, contained mainly an acid of the composition of dibrommaleic acid.

In the mother liquors from the baric dibrommaleate there appeared to be a trace of a more soluble barium salt beside baric bromide; but its quantity was too small to admit of separation and analysis.

The oily residue left undissolved by water gradually solidified upon standing. Cold chloroform dissolved the greater portion of it, leaving a small quantity of short, prismatic crystals. Upon evaporation of the chloroform, an oil was left, which gradually solidified in masses of radiated prisms, contaminated with a small quantity of an oily impurity whose nature could not further be determined. After several crystallizations from alcohol, this substance melted at 55–56°, and when treated with baric hydrate gave the characteristic reactions of mucobromylbromide. It was still further identified by analysis.

0.2280 gram substance gave 4000 gram AgBr.

Calculated for $C_4HBr_3O_3$.		Found.
Br	74.77	74.68

The prismatic crystals, which were sparingly soluble in cold water and chloroform, were recrystallized from hot water, and showed then the characteristic properties of ordinary dibromsuccinic acid. On heating, they remained unaltered till the temperature had risen to over 200°; at a somewhat higher point they had completely volatilized. The sublimate condensed in the colder portions of the tube in oil drops, which gradually solidified. The melting point of the solid thus obtained, after pressing with filter paper, was found to be 126°. According to Fittig and Petri,[1] the sublimate formed under the same conditions from dibromsuccinic acid has the

[1] Ann. Chem. u. Pharm. **195**, 58.

melting point of monobrommaleic acid (128°). The quantity of dibromsuccinic acid formed in this reaction was quite small.

0.2855 gram substance gave 0.3880 gram AgBr.

Calculated for $C_4H_4Br_2O_4$	Found.
57.97	57.83

When the original product of the reaction was treated at once with dry chloroform, the greater part was instantly carried into solution; and the dibromsuccinic acid, together with a small quantity of mucobromic acid, were left undissolved. The filtered chloroform solution, when shaken with a few drops of water, gradually solidified with separating crystals of dibrommaleic acid; so that the original product must have contained the dibrommaleic acid as anhydride.

The two main products of the reaction were, therefore, dibrommaleic anhydride and mucobromylbromide. The relative weights of these two products were such as to suggest at once the equation:

$$2C_4H_2Br_2O_3 + Br_2 = C_4H_2Br_2O_4 + C_4HBr_3O_2 + HBr,$$

when the dibrommaleic acid would readily pass into its anhydride. The weights obtained in successive preparations were, however, found to vary so much that I am inclined to consider the anhydride as the direct product of the reaction, and the mucobromylbromide a secondary product formed by the action of the hydrobromic acid set free. In either case, the formation of dibromsuccinic acid can hardly be explained without assuming a reducing action of the hydrobromic acid, like that which is normal to hydriodic acid. Although reductions of this sort by the action of hydrobromic acid have seldom been noticed, the conversion of tartaric acid into monobromsuccinic acid by this means, noticed by Kekulé[1] in 1864, would seem to be perfectly analogous.

[1] Ann. Chem. u. Pharm. **130**, 30.

(*To be continued.*)

CHLORO-BROMIDE OF LEAD.

By Malvern W. Iles.

In the treatment of the Leadville carbonate ores by the blast furnace, the writer has noticed a number of very curious and interesting compounds. The facilities here offered for an extended observation are unusually good, inasmuch as the Grant Smelting Co. works have a capacity for treating no less than 150 to 200 tons of ore per day, and an opportunity is offered for collecting furnace products from seven different furnaces.

A compound having the formula Pb(BrCl) has recently been discovered, occurring as a furnace product, in small (2½ inch) circular openings, in the cast-iron supporting plate 11½ inches above the water-jacket. The iron ring rests upon four cast-iron columns, and supports the sheet-iron fire-brick lined structure above. This ring-plate is perforated by holes, which serves to prevent a total rupture of the plate by the expansion caused by the internal heat.

The courses of fire-brick at the boshes close these holes from below, whilst the interior fire-brick lining covers these circular openings, thus forming a small condensation chamber in which the chloro-bromide of lead was found.

As neither Dana nor Naumann makes mention of this compound, and we have been unable to find any description given in any work at our disposal, we feel justified in stating such physical and chemical observations as we have noticed in our investigation.

In order to see whether this compound was contaminated with any silver salt, it was assayed, $\frac{1}{10}$ assay ton yielding by cupellation only a most minute trace. Hence it is to be concluded that this was simply an accidental occurrence of a small amount of ore, or a trace of a volatile silver salt.

We have recently noticed that the white fumes that condense upon the surrounding cool objects in the vicinity of the slag tap-hole yield 3½ ounces of silver per ton; hence it is not improbable that there is some volatile compound of silver not clearly identified, and which slightly mingles with the chloro-bromide of lead.

Properties.

The furnace crystals occurred in several forms, as for example, in pure white, delicate, dendritic plates, not unlike crystals of lead

chloride; in long acicular needles, in semi-fused distorted needles having a slightly yellowish tint, and also in entirely fused warty masses.

It dissolves in warm water, forming a milky white turbidity which readily clears up on the addition of a few drops of nitric acid. The aqueous solution deposits plate-like crystals, and from the moderately dilute solution, by slow crystallization, one may obtain doubly terminated acicular needles, considerably thickened in the central portion.

It sublimes on charcoal, giving a white coating. In a closed tube it melts readily to a bright red color; upon cooling it lightens up, changing from a lemon yellow to a pure white. On increasing the heat it sublimes in heavy oily drops. Density 5.741.

This product is found to be very stable, and is decomposed by boiling concentrated sulphuric acid, only by repeated applications, and the complete transformation into a sulphate is difficult.

ANALYSES. *Chlorine + Bromine.*

.559	gram	salt	gave	.573	gram	(AgBr+AgCl)	= 35.714	per ct.	(Br+Cl)
1.251	"	"	"	1.2825	"	"	"	= 35.718	"	"
1.251	"	"	"	1.277	"	(fused)	"	= 35.566	"	"
		Average of three determinations,						35.666	"	"

Lead.

.559	gram	salt	gave	.513	gram	$PbSO_4$	= 62.695	per cent.	Pb.
1.086	"	"	"	.996	"	"	= 62.717	"	"
1.251	"	"	"	1.167	"	"	= 63.729	"	"

The first and second determinations were made upon the furnace product, while the substance used for the last determination was the result of purification by crystallization from an aqueous solution.

Bromine.

1 gram fused (AgCl+AgBr) gave a loss on passing dry pure chlorine gas over the salt, in a bulb tube, of .141 gram = .595055 gram AgBr = 25.321 per cent. Br.

The formula Pb(BrCl) requires Pb=64.186 per ct. and (Br+Cl) = 35.814 per cent. We may state our results as follows:

Found.		Calculated.	
Pb	63.729 per cent.	Pb	64.186 per cent.
Br	25.321 "	Br	35.814 "
Cl	10.345 "	Cl	
	99.395		100.00

The mixed silver salt was readily prepared by making an aqueous solution (aided by a few drops of nitric acid), and adding silver nitrate; after purification by washing with hot water the salt was dried and analyzed. 0.570 gram (AgCl+AgBr) was mixed with pure granulated lead and cupelled in the assay muffle, of course after scorification, and the usual precautions taken for rich chloride ores. The weight of the silver button was .36345 gram, which corresponds to 63.763 per cent. silver; theoretical percentage for formula = 65.158 per cent.

A chloro-bromide of silver, or embolite, has been described and analyzed by Prof. Th. Richter[1] which closely corresponds to the above compound, termed *megabromite* by Breithaupt.

Prof. Richter's analyses gave Ag=64.19 per cent., Br=26.49 per cent., Cl=9.32 per cent. The ratio of the bromine to the chlorine 1 : 0.8, whilst we found in the compound under consideration a ratio of 1 : 0.92.

Inasmuch as the furnaces from which the chloro-bromide of lead was collected had been in blast for some time, it is reasonable to conclude that the chloro-bromide of silver existing in these ores has the same general composition as shown in the above haloid silver salt. While we do not deny the probability that the chloro-bromide of lead may have existed in the ores as such, yet it can readily be seen how a decomposition may have taken place in such a manner as to produce this lead salt, since it is a well known fact that heated metallic lead will decompose all known salts of silver. In conclusion we may state that samples of this compound have been forwarded to Professors Richter, Dana, Remsen, Chandler and others.

[1] Berg- und hüttenmännische Zeitung, **18**, 449.

Chemical Laboratory, Grant Smelting Co., Leadville, Colorado.

Laboratory Notes from the University of Cincinnati.

XIX.—ALKALIMETRY WITH PHENOL PHTHALEIN AS INDICATOR.

By R. B. Warder.

The properties of phenol phthalein, including the magnificent red color which it yields with alkalies, were described by Baeyer[1] in 1871; but Luck[2] seems to have been the first to use it as an indicator. With caustic alkalies the delicacy of the reaction is marvelous; but when carbonates are present, the change of color takes place more gradually, and cold solutions of an acid carbonate are not colored at all. Even the carbonic acid of the atmosphere may have a marked influence.

For the following experiments a weighed quantity of a dark colored sample of phenol phthalein from Kahlbaum was dissolved in weak alcohol, and a roughly graduated dropping tube was inserted in the stopper of the flask containing the solution, by which any required quantity of the indicator could be approximately measured out. 0.1 milligram of commercial phthalein was added to 100 cc. distilled water, and $\frac{1}{100}$ normal NaOH solution was run in from a burette. With 0.4 cc. $\frac{1}{100}$ n. alkali, the color was barely perceptible; with 1 cc. it was distinct, with 2 cc. a beautiful faint pink color was produced, which deepened to a distinct crimson red with 4 cc. of the alkali. The color produced by one or two cc. could easily be discharged by shaking with air, and that produced by 4 cc. was entirely discharged by less of my own breath than a single expiration; indeed, this experiment is well adapted for lecture demonstrations of the carbonic acid of the breath, being much more striking than the usual lime-water test. With different samples of ordinary distilled water, a varying amount of alkali was required to produce the succession of tints above described; the first appearance of color is often very transient. The least quantity of alkali is required with water from which the carbon dioxide has been carefully expelled by heat, and it is convenient to have a supply of such water at hand in a well stoppered flask.

As a further test of the delicacy of this indicator, 20 cc. of $\frac{1}{2}$

[1] Ber. d. ch. G. **4**, 658.

[2] Zeitsch. anal. Chem. 1877, 332.

normal alkali were carefully neutralized with oxalic acid (with boiling to expel CO_2), then diluted to about 100 cc., and with the aid of 0.4 milligram phthalein a distinct tint was produced by the addition of 1 cc. of $\frac{1}{100}$ normal NaOH, and a beautiful pink color by less than 2 cc. Hence, a variation of less than 0.1 per cent. of the whole quantity of alkali used produced a marked change even in very dilute solution; with concentrated solutions the delicacy is much greater.

On adding acid to a cold dilute solution of sodic carbonate we may suppose the first reaction to take place thus:

$$2Na_2CO_3 + C_2H_2O_4 = C_2Na_2O_4 + 2HNaCO_3;$$

and as a solution of $HNaCO_3$ gives no color with phthalein until it is decomposed by heat, we might expect the reddened solution of a carbonate to be entirely decolorized by $\frac{1}{2}$ equivalent of acid. I have been able to realize this expectation only in part, yet the facts indicated serve as a basis for a method for the estimation of causticity of solutions which do not contain too large a proportion of carbonate. The alkaline solution, with a suitable quantity of phenol phthalein, is mixed with standard acid, in the cold, until the red color either vanishes entirely, or (if the reaction is lacking in sharpness from the presence of carbonate) until the color is extremely faint. Of course the solution must be sufficiently dilute to avoid any danger of effervescence in this first titration. The changes of tint closely resemble those observed when a solution of rosaniline is greatly diluted, and it is a valuable aid to the eye to keep such a solution at hand for comparison; and as the depth of color at this stage varies with the quantity of indicator used, it is desirable to take some definite amount. After completing the first titration, the mixture is boiled thoroughly with successive additions of more acid, until the last returning trace of red color is discharged by a single drop; or the end may be more quickly reached (in accordance with the law of the "action of mass") by boiling at once with excess of acid, and completing the titration with the aid of caustic alkali. The end reaction in this case, which is very sharp, is marked by total discharge of color.

Let A_1 = the acid required in first titration, and A_2 = that required in the second, with any needed deduction for the alkali used near the end; then $A_1 + A_2$ represents the total alkali; $A_1 - A_2$ represents the caustic alkali; $2A_2$ represents the carbonate.

The following titrations were made to test this method. Solutions used were: A, oxalic acid, 0.991 normal; B, standard sodic carbonate, ½ normal; C, sodic hydrate, nearly ½ normal. 0.2 milligram phenol phthalein was used in each case.

The caustic soda was prepared by dissolving metallic sodium in water from which the carbon dioxide had been expelled. It was kept in a vessel provided with soda-lime ventilator, and was drawn without contact with the laboratory atmosphere, through the lower end of an ordinary burette, which was also provided with a soda-lime ventilator at the top.

Notwithstanding these precautions, a trace of carbonate appeared to be present in solution C, or to be formed during titration; for 42.22 cc. of C were exactly decolorized in the cold by 21.39 cc. of A; on boiling, the color returned, and a further addition of .06 cc. of the acid was required. By the formula given above, the caustic alkali present represents 21.39—.06=21.33 cc. of A, or 21.14 cc. of perfectly normal acid. Hence we may assume that its strength in NaOH is $1.0014 \times \frac{1}{2}$ normal with an admixture of Na_2CO_3 in the quantity used, equivalent to $2 \times .06 = .12$ cc. of normal solution. Various mixtures of B and C were then titrated in the same manner. The following table expresses the volumes of these solutions used, as measured from burettes. A_1 is the quantity of acid required in the first titration, A_2 is the additional amount required when the solution was boiled:

	B	C	A_1	A_2	A_1+A_2	A_1-A_2	$2A_2$
(1)	2.53	41.70	21.71	.69	22.40	21.02	1.38
(2)	4.90	39.65	21.33	1.30	22.63	20.03	2.60
(3)	9.85	38.04	21.74	2 56	24.30	19.18	5.12
(3′)	"	"	21.80	2.50	"	19.30	5.00
(4)	10.61	38.23	22.12	2.64	24.76	19.48	5.28

The following table shows the total alkali, the caustic alkali and the carbonate taken, as represented in columns B and C, together with the corresponding quantities found by means of A_1+A_2, A_1-A_2 and $2A_2$. For convenience, these quantities are not calculated by weight, but are represented in cc. of normal solution, as the object is merely to exhibit the experimental errors incident to this method. It is allowable to assume, in calculating these results, that each portion of C used contained the same quantity of Na_2CO_3 that was found in the preliminary titration:

	Total Alkali.		NaOH.		Na_2CO_3.	
	Taken.	Found.	Taken.	Found.	Taken.	Found.
(1)	22.25	22.20	20.86	20.83	1.38	1.37
(2)	22.41	22.43	19.84	19.85	2.57	2.58
(3)	24.08	24.08	19.03	16.01	5.04	5.07
(3′)	"	"	"	19.13	"	4.96
(4)	24.55	25.54	19.13	19.30	5.42	5.23

Two values of A_1 and A_2 are given for the third experiment. Those in line (3) correspond to a reading taken, while there was still a faint reddish tinge, while (3′) represents a complete discharge of color in the first titration. The difference is not great, but a little practice will enable the operator to obtain still closer results. In experiment (4) the color was quite inappreciable when the reading was taken; and the result shows that A_1 was rather too large and A_2 too small.

The use of phenol phthalein as an indicator, so strongly recommended by Luck, seems to have been somewhat neglected in consequence of the very property which is the basis of the method just described for distinguishing alkalinity and causticity. I think the convenience and accuracy of the new method will recommend it to those who have occasion to make such determinations; but, as its capabilities are not yet exhausted, I hope to continue the investigation, and ascertain whether the plan can be modified for the detection and estimation of carbonic acid in general.

March 10, 1881.

REVIEWS AND REPORTS.

Brief Review of the most important Changes in the Industrial Applications of Chemistry within the last few Years.

[*Continued from Vol.* **2**, *p.* 426.]

Artificial Production of Heat for Domestic Purposes.

The manufacture of artificially compressed blocks of solid fuel from the otherwise waste bituminous coal which has been crushed to dust in the process of extraction, has been largely extended of

late years, though the proportion of such fuel in use is small as compared with other materials.

The cheapest form of liquid fuel—crude petroleum—has been tried in many forms of stoves and burners, for warming of rooms, cooking, and other domestic purposes, but the difficulty of securing complete combustion, the consequent odor not only in the neighborhood of the fire, but often attaching itself to articles of food cooked by it, and the serious danger attending the storage, pouring, and use of such a liquid in unskilled hands, have proved themselves objections sufficient to prevent any general or very extensive adoption of this heating agent. Its true field of future use, notwithstanding the limited success which has hitherto resulted from experiments in this direction, seems likely to be found on board armored war vessels as the source of motive power beneath the boilers of marine engines; its great heat-producing power for given weight, freedom from ash, sulphur and other impurities, compactness of stowage, economy resulting from the complete control over consumption, the facility and quickness with which the supply may be taken on board or discharged, and other peculiarities, giving it immense advantages over ordinary coal. The like reasons render it not improbable that petroleum-burning locomotives may yet be successfully constructed.

"Water gas" or "hydrocarbon gas," resulting from the reaction of steam upon glowing carbon in some cheap form, shown by Siemens to be producible with great economy by means of his "generator" or analogous arrangements, has been used to some extent for domestic heating, and offers advantages which seem likely to be more generally appreciated in the future than they yet have been. Much remains to be done in working out the details of proper arrangements for storing, distributing and using the vast volumes of such gas which would have to be dealt with if its use should become general in even a single large city, and the possibilities of mischief from its highly poisonous character would require well considered precautions against its escape in an unburnt state, but it may fairly be said that such difficulties are not at the present day nearly so formidable as those which seemed to oppose the introduction of coal gas for illuminating purposes seventy or eighty years ago. The question of using gaseous fuel for domestic heating has assumed new interest of late in London, where the strong feeling anciently entertained against bituminous coal on account of its smoke and "stench," as testified to by royal proclamations, petitions to Parliament, and other public documents in the 15th, 16th and 17th centuries, has been revived amidst the great population over which a gloomy winter atmosphere broods upon the banks of the Thames. The practical ingenuity of Dr. C. W. Siemens has been very recently shown in his suggestion[1] of an efficient form of grate for burning gas, intended and apparently well calculated to

[1] Nature, Nov. 11, 1880, p. 25.

avoid the difficulties which have presented themselves in using such fuel. The price, which may well be called extravagant, paid by consumers of ordinary coal gas in American towns, and even cities, precludes here its use as proposed by Dr. Siemens, but there is no valid reason against the production of generator gas at a cost which would make it a thoroughly economical source of heat. Another suggestion has lately been made as to the suppression of a smoky atmosphere in cities burning bituminous coal, namely, that the whole supply of such coal should be partially coked at a low temperature, so as to obtain a very rich gas for illuminating purposes, with abundant and valuable tar products, leaving a semi-coke behind for use as domestic fuel, which it is assumed might be burned with little or no escape of smoke. This idea seems complicated with many more doubtful conditions than that of adopting for general use the generator gas.

Other important and interesting questions in relation to the future supply of heat to our dwellings must be dismissed as not chemical but physical in their character, such as the distribution to many houses of heat from central stations by means of steam pipes, lately brought into experimental use on a working scale in this country, the transmission of mechanical energy for moderate distances by such contrivances as Hirn's telo-dynamic wire with subsequent conversion into heat, the transmission and conversion of cheap electricity, itself derived from the heat of burning fuel by means of dynamo-electric engines, the more direct storing up and utilization of sun heat, particularly that of low temperature, etc., etc.

For *cooling* the air of dwellings in hot climates the more efficient ice machines of the last twenty years have been to a limited extent resorted to. In addition to the various volatile liquids used singly which have been alluded to in an earlier part of this report as employed in working these refrigerating machines, it has been lately proposed to use a mixture of ether or methyl chloride with sulphur dioxide or ammonia, taking advantage of the solvent action of the former bodies on the latter to work at lower pressures than would otherwise be necessary.

Artificial Production of Light.

Candles.—The two principal directions of advance in the procurement of crude materials for candle-making have for some years been, the importation of larger and larger supplies of vegetable oils and waxes from the hotter regions of the globe, and the more extensive and skilful extraction of fatty matter from waste residues of various sorts. Under the former head palm oil and coconut oil—particularly the former—still hold the first place, but shea butter, carnauba wax, and sundry other materials have come more or less into use.

Under the latter head slaughter-house scraps and refuse, the bodies of dead animals from the streets of cities, condemned meat,

bones to be afterwards used for glue making or for bone-black, the skimmings of liquid sewage, the dirty packing removed from railway axle-boxes, greasy cotton waste which has been used for wiping machinery, soap-water from laundries and private houses, refuse from the clarification of olive and colza oils, etc., etc., have been brought into requisition, and by means of heat, pressure, solution in carbon disulphide or light petroleum hydrocarbons, and treatment with small quantities of acids and alkalies, have been made to yield important supplies of fatty material, partly to be used as such and partly to undergo conversion into pure and clean mixtures of the fatty acids. In the Southern United States the rapid growth of the cotton-seed oil industry is worthy of note, although the product goes largely into use in other hands than those of the candle-maker.

In the important manufacture of the fatty acids the three processes now chiefly in use are, 1st. Decomposition by means of sulphuric acid, and distillation with the aid of superheated steam. 2d. Saponification by lime in closed vessels under pressure, and decomposition of the lime soap by sulphuric acid. 3d. Saponification by lime as before, followed by treatment with a small excess of sulphuric acid, and distillation in a current of superheated steam.

The relative advantages of these processes under different conditions have been discussed by Prof. De Wilde in the Belgian official report upon the Paris Exhibition of 1878. Lime is chiefly used by the smaller manufacturers; sulphuric acid, followed by distillation, in the largest establishments. By far the most interesting novelty in this field of industry is the appearance in the market, introduced by two French manufacturers, of palmitic acid, artificially made from oleic acid by heating with strong potash lye at 300° to 325° C., thus producing potassium palmitate and acetate, to be separated by washing with a limited quantity of water, the former salt to be then decomposed by sulphuric acid. The quantity of caustic potash required is said to be large—twice the weight of the oleic acid to be treated—but it is recovered, the acetate of potassium being calcined and converted into carbonate, to be causticized with lime, while the palmitate is either decomposed by sulphuric acid, as just mentioned, and the sulphate of potassium converted into carbonate by the Leblanc process, or palmitate of calcium is formed by heating with lime under pressure, caustic potash being thus directly reproduced, and the lime salt afterwards decomposed by sulphuric acid. The value of the principal by-product of the fatty acid manufacture, glycerine, constantly increases, as its useful properties are applied in new directions and upon a continually larger scale. As a solvent in pharmacy, in connection with perfumery and various articles of food, as a preservative of animal and vegetable substances from decay, as an ingredient in the manufacture of beer, as the means of keeping moist and soft such articles as chocolate, tobacco and soap, as preserving the pliancy of leather and maintaining the softness and

delicacy of the living skin, as a lubricant, in admixture with water to guard gas-meters against stoppage by freezing, as the material for making nitro-glycerine, and in sundry other directions this substance, twenty-five years ago but little known or used, has acquired an important place in general consumption. While its price has been greatly lowered, the state of purity in which it is placed upon the market has been improved until now there is little left to be desired in this regard.

The manufacture and purification of solid paraffine have rapidly developed, and new sources of supply have been resorted to The comparatively small proportion of such solid hydrocarbons existing in the thinly fluid petroleum of Pennsylvania is in the hands of some refiners carefully collected, by freezing out and pressure, from the heavier lubricating oils, and by regulated washing with petroleum spirit brought to a beautiful condition of whiteness. The thick and heavy petroleum of the Caspian and of Burma is largely worked, and yields a much more considerable product, and the ozokerite of Austrian Gallicia has for the last twenty years added greatly to the general supply of analogous material, the purified "ceresine" obtained from it justifying the name by a nearer resemblance to beeswax than is presented by any other such material of mineral origin. The great hardness and high fusing point of this mineral wax when it has been simply purified are remarkable and valuable; when the crude material is submitted to distillation, products more nearly resembling the true paraffines of the $C_nH_{2n}+_2$ series are obtained. Furthermore, the production of paraffine for candle-maker's use by destructive distillation of such materials as Boghead coal, certain lignites, such as the Schweelkohle of Saxony and Thuringia, and bituminous shales, is carried on with success, serving to continue the use of these crude substances beyond the time at which their distillation for liquid illuminants would have ceased to be profitable.

Incidentally may be mentioned here the recent growth of the manufacture, and wide extension of the use, of such semi-solid products as are sold under the names "vaseline," "cosmoline," etc., derived from the later residues of petroleum distillation, and in purified form intended to serve as substitutes for lard and other fats in the preparation of salves and ointments, in dressings for surgical and veterinary practice, as a vehicle for perfumes in making "pomades" for the hair, and as an application to leather with a view to preserve its flexibility. The objection arising from petroleum-like odor has been successfully removed, and the insusceptibility of these products of rancidity gives them real value.

Liquid Illuminants for burning in Lamps.— Doubtless no natural substance has been within the last twenty years added to the world's store of crude materials equal in importance to liquid petroleum. Immense as the supply has previously been from the United States, it has for the last two or three years not only shown no sign of falling off, but has actually exhibited an enormous

increase. Among foreign sources of supply the Russian petroleum region of the Caucasus has acquired greatly increased commercial importance. In regard to the product from this district the interesting fact seems lately to have been made out that it consists largely of a mixture, not of true paraffines, nor of members of the olefine series, but of hydrocarbons, isomeric with the latter, which may be viewed as addition derivatives of the aromatic series, such as C_6H_{12}, etc. The same may be true of the Gallician ozokerite, which is said to afford the empirical formula C_nH_{2n}, and, in very small quantity, these aromatic hydrocarbons have also recently been detected in American petroleum. The refining of petroleum is a comparatively simple process, but has been improved in details, and in the care with which these are carried out, so that the best "kerosene" for burning is a beautifully colorless, clear, limpid liquid. The chief desideratum for the refiners is the discovery of a sufficiently extensive use for the lighter and more volatile products of distillation, known as "petroleum spirit," "gasoline," "benzine," etc. Although these materials have come largely into use as solvents and for some other purposes, their consumption is still insufficient to absorb profitably the immense quantities produced. Hence the temptation to allow an undue proportion of the highly volatile hydrocarbons to remain in commercial kerosene, to mix the two after they have been separated by distillation, and even to substitute the former for the latter under various flimsy pretences of rendering the material "inexplosive." Much ingenuity has been bestowed upon the various devices for testing the safety of kerosene oil, and minute instructions have been drawn up for their use, but, although the process is essentially a very simple one, it requires practice, an honest desire to obtain trustworthy results, and above all a clear comprehension of the chemical and physical principles involved. Great improvements have been made in lamps, particularly in those intended for burning petroleum, the shape and proportions of the burners and chimnies being much superior to those of the earlier lamps used for this illuminant.

Illuminating Gas.—There has been no radical change for some time past in the method of manufacture of ordinary coal gas. Where systematic public inspection is practiced, the production of gas of higher illuminating power, and in the hands of those aiming at improvement, the tendency to more careful purification, and better utilization of by-products, have been chiefly noticeable. The Laming mixture, in which ferric hydrate is the principal ingredient, has passed into more extensive use in the purifiers than formerly, though lime is still employed. Liebermann has recently suggested a new mode of removing the vapor of carbon disulphide, which tends so obstinately to remain in the gas under existing systems of purification,—namely, by taking advantage of the eagerness with which this vapor is absorbed by solid paraffine, which may be used in the crude state, and from which the carbon disulphide may be easily recovered by distillation. It would be important to ascertain

whether the luminiferous hydrocarbons would not also be absorbed to such an extent as materially to lower the value of the gas; that benzole, which Berthelot has found to be the chief illuminant in Parisian gas, is so absorbed by paraffine is stated by Liebermann himself. The suggestion has already been noticed that the whole of the bituminous coal used in English cities as fuel should be subjected to incomplete destructive distillation at low temperatures, so as to leave a kind of coke assumed capable of burning without objectionable smoke, while very rich illuminating gas would be obtained in great abundance. The great disturbance of values for the solid fuel residue, the gas, and the tar products, which carrying out such an idea would entail, makes it difficult to form even an approximate estimate of the net economic result. Very real improvement has been made within the last few years in the arrangements for using coal gas, notably as regards the details of construction of the burners, and the due regulation of the pressure under which the gas escapes.

Pettenkofer has shown how gas of fair illuminating quality may be made from wood or peat, by distillation at quite low temperature, and carrying the volatilized products through a second retort or "generator" at much higher temperature.

Crude petroleum has been employed by various inventors as material for the production of permanent gas, but its use cannot be said to have got beyond the field of experiment.

The production of "water-gas" by bringing steam in contact with red hot solid fuel, and afterwards rendering luminous the gaseous mixture so produced by causing it to take up the vapor of some of the heavier hydrocarbons, has been many times revived in more or less improved forms, and of late with a very notable measure of economic success.

In the United States the combustion from ordinary gas fixtures of the most volatile portions of petroleum-gasoline, or light petroleum spirit—carried along as vapor by a current of air produced by simple mechanical contrivances—has been brought extensively into use, but the results are far from satisfactory, both on account of the danger attending the handling the gasoline itself by ignorant people, and from the annoying variability of the extent to which the vapor is formed or condensed under varying conditions of atmospheric temperature. The comparatively high density of the hydrocarbon vapor is a further disadvantage, as invisible trains of combustible material are liable to be formed from burners left open but a short time, which may blaze up dangerously from lights placed at a much lower level.

The valuable process of Tessié du Motay for cheaply preparing oxygen gas, and the various modes of using it in connection with illumination, whether by throwing jets of mingled oxygen and hydrogen or "water-gas" upon pencils of refractory solids, or by introducing oxygen into hydrocarbon flames rich in carbon, have not established themselves in general use, but are still capable of being occasionally resorted to, with advantage, under special conditions.

Illuminating gas compressed to a tension of about six atmospheres in tinned iron cylinders has come into use as the most convenient means of rendering gas lighting portable, as in railway carriages, on board steamships, &c.

It is needless to say that the greatest amount of interest in questions of illumination has of late attached to the use of electricity, applied either to the production of the "galvanic arc," or to maintaining the incandescence of a slender rod of carbon or other refractory material. Although the most important features of the problem of electric lighting are of purely physical character, not suitable for discussion in this report, some minor matters of chemical interest have from time to time been brought forward. A noteworthy example of mixed chemical and physical principle is afforded by the recently invented Maxim lamp, in which the integrity of the slender strip of incandescent carbon is secured, at any rate for a long time, by enclosing it, not in a vacuum, but in an atmosphere of gasoline vapor, the deposition of carbon from which tends to strengthen the parts of the slip originally weakest by these becoming most strongly heated at first. It may be remarked in passing that probably no subject of scientific and industrial interest has, for a long time, been so much discussed in public as electric lighting, with such remarkable neglect of the most fundamental and simple principles involved, both of scientific truth on the one hand and of economic conditions on the other; and this has in many instances been true, not only of mere newspaper discussion and common conversation, but of the utterances of men who ought not to have been ignorant of, and presumably were not ignorant of, the considerations they neglected.

As an interesting and practically valuable contribution to our methods of obtaining light under special conditions may be mentioned in conclusion the "luminous paint" patented by Balmain, and lately brought into the market by Ihlee and Horne of London. This revival in industrial form of the "phosphori" which attracted so much attention from the chemists of the 17th and 18th centuries seems destined to a really useful place in the service of man in the future, though the extent of its utility can perhaps hardly yet be foreseen. The principle of its light-storing power is physical, but the actual production of the sulphide of calcium, which seems to be the essential material used, is a process of chemical manufacture.

Appendix to Production of Heat and Light.—Matches.

In the production of these useful little articles the use of round splints of wood, made by end-on compression of wood through a perforated steel block, has for many years generally replaced the rougher sawn or cleft splints, at any rate for all but the coarsest matches, and for the preliminary tipping sulphur is seldom now employed, its place having been taken by stearic acid or paraffine.

Red or amorphous phosphorus, after having for a time been in-

troduced to a considerable extent into the composition of the principal tipping, has been pretty generally abandoned in favor of the longer known, cheaper, and more easily combustible crystalline form of the element. In the composition used in making some of the Swedish matches, potassium pyrochromate furnishes a portion of the oxygen along with the more active chlorate or nitrate of potassium.

"Safety matches," capable of being ignited only by friction upon a specially prepared surface, may be counted as a comparatively recent branch of the manufacture; the active materials used being generally antimony sulphide or sulphur and potassium chlorate on the match, and amorphous phosphorus with pulverized glass on the surface of the box. At the Philadelphia Exhibition of 1876, safety matches of American manufacture were shown which dispensed altogether with the use of phosphorus, the match being tipped with a composition containing sulphur, red lead, and potassium chlorate, while the prepared surface on which it was to be struck consisted of hard vulcanite with which a large proportion of antimony sulphide had been incorporated.

J. W. MALLET.

(*To be continued.*)

REPORT ON ANALYTICAL CHEMISTRY.

[*Continued from Vol.* **2**, *p.* 204.]

Oxygen.—As previously reported,[1] Tiemann and Preusse, in their comparative examination of the three methods usually employed for the determination of the oxygen absorbed by water, found that the results obtained by the method of Bunsen and that of Schützenberger were nearly concordant, while those obtained by the method of Mohr were uniformly too low. These conclusions were not in accord with those reached by J. Koenig and L. Mutschler,[2] who stated that the methods of Bunsen and Mohr yielded closely agreeing results, and recommended that the method of Schützenberger be discarded. The objections to the method were: 1. The instability of the standard solution of hydrosulphite; 2. The want of uniformity in its action upon free oxygen contained in water and upon the oxygen of ammoniacal cupric and iron-alum solutions by means of which it is usually standardized; 3. The want of uniformity in its action in aqueous solutions of oxygen of different degrees of concentration.

Koenig and C. Krauch[3] have now published the results of a reinvestigation of the subject. Their conclusions are: 1. That the absorption coëfficient of air for distilled water as determined by Bunsen, which has hitherto been relied upon as the standard for

[1] This Journal, **2**, 67. [2] Berichte d. deutsch. chem. Gesell. **10**, 2017.
[3] Zeitschrift analyt. Chemie, **19**, 259.

testing the correctness of the results obtained by the different methods, is not in all cases to be depended upon; 2. That the method of Mohr gives results which are uniformly too high, instead of too low as stated by Tiemann and Preusse; 3. That, contrary to the conclusions of Tiemann and Preusse, the method of Schützenberger gives results which are always too low; 4. That, though neither the method of Mohr nor that of Schützenberger gives absolutely correct results, either can be successfully employed to determine the relative amounts of oxygen contained in different waters. But if the latter is used, the hydrosulphite solution must be standardized by means of an aqueous solution of oxygen of known concentration and not by means of an ammoniacal cupric or an iron-alum solution.

Ozone.—Em. Schoene[1] calls attention to the fact that, since the existence of hydrogen superoxide in the air has been demonstrated, the occurrence of ozone as a constituent of the atmosphere has become very doubtful. Most of the reactions formerly relied upon for the detection of ozone are also produced by hydrogen superoxide. The latter liberates iodine from the iodides and oxidizes thallous compounds. It does not oxidize manganous salts, but such oxidation cannot be regarded as an evidence of the presence of ozone, since ordinary oxygen in the presence of carbonate of ammonium—which is always to be found in the air—will effect it. The tarnishing of silver may be, and probably always is, due to the presence of sulphides.. The odor sometimes observed and ascribed to ozone is at best a questionable argument for its presence. Most observers would be liable to confound the odors of ozone and hyponitric acid. Moreover, ozone is not produced by the electric spark in a mixture of oxygen and nitrogen, but only oxide of nitrogen, hence the fact of visible electric discharges in the air is no evidence of its formation. It is produced by the silent discharge, but of this, as an atmospheric phenomenon, we still know too little to justify us in regarding it as a probable source of supply.

Water.—Fr. Rüdorff[2] has described a simple and convenient apparatus for the determination of the aqueous vapor of the air by absorption. It consists of a flask of the form of an ordinary triple-mouthed Wolff's bottle, and has a capacity of about 1000 cc. Each of the three apertures is fitted with a ground glass stopper. One of these stoppers carries a bent glass tube which serves as a manometer, another a finely graduated burette for sulphuric acid, and the third a glass tube to connect the interior of the flask with the outside air. The manometer, burette and glass tube each contain a glass stopcock situated just above that portion of them which forms the stopper. The liquid used in the manometer is sulphuric acid having a specific gravity of 1.3, which, at ordinary temperatures, neither gives up nor absorbs an appreciable amount of water. The burette is filled with concentrated sulphuric acid. To deter-

[1] Berichte d. deutsch. chem. Gesell. **13**, 1503. [2] Ibid. **13**, 149.

mine the aqueous vapor in any specimen of air filling the apparatus, the stopcocks of the manometer and the glass tube are closed, that of the burette opened and a small quantity of sulphuric acid allowed to flow in. The stopcock belonging to the manometer is then opened, whereupon the dilute sulphuric acid rises in the limb nearest to the flask in consequence of the diminished internal pressure. Lastly, sulphuric acid is added from the burette until equilibrium is restored in the manometer. The volume of sulphuric acid used is equal to the volume of aqueous vapor originally present.

Other, but certainly not superior, forms of apparatus for the estimation of aqueous vapor by absorption have been proposed by A. van Hasselt[1] and A. Matern.[2]

Hydrogen Superoxide.—Em. Schoene[3] recommends the use of thallium papers for estimating the "oxidizing principle" of the atmosphere, which, since the existence of ozone in the air has become doubtful, he believes to consist mainly and perhaps wholly of hydrogen dioxide. The oxidation of the thallous compounds is not dependent on the presence of moisture. Moreover, the oxidized papers can, with proper care, be preserved for any length of time and thus afford a visible record of observations made. They are best prepared by saturating, not more than two or three days before use, strips of Swedish filter paper with a solution containing in each 100 cc. 10 grams of thallium hydroxide, and drying as quickly as possible in the air. They are then preserved until wanted in closed vessels over burned lime. The defects of the methods of observation which depend upon the liberation of iodine from iodide of potassium (Schoenbein's and Houzeau's), are such, he thinks, as to render them wholly unfit for use. The quantity of iodine liberated depends upon the amount of moisture present, hence the "ozonometer" of Schoenbein, as can be demonstrated, is nothing but a crude hygrometer; also upon the hygroscopic condition of the materials employed in preparing the papers, hence papers obtained from different sources, though prepared in the same manner, are unequally affected when exposed together under the same conditions.

Halogens.—In order to obtain a nearly constant current of hydrochloric acid gas, L. L. de Koninck[4] uses solid chloride of ammonium and concentrated sulphuric acid. The same author[5] recommends for oxidizing purposes a solution of bromine in water, containing ten per cent. of bromide of potassium.

According to A. Jorissen,[6] minute quantities of iodine in bromine may be detected by the following method: A few drops of the bromine to be tested are placed in a porcelain dish, 30 cc. of a cold saturated solution of chlorate of potassium added, and heat applied until all color has disappeared. After cooling, the solution is

[1] Zeitschrift analyt. Chemie, **19**, 67. [2] Pogg. Annalen, N. F. **9**, 147. Also **10**, 149.
[3] Ber. d. deutsch. chem. Gesell. **13**, 1508. [4] Zeitschrift analyt. Chemie, **19**, 467, 468.
[5] Ibid. **19**, 353.

treated with a few drops of a solution of sulphate of morphine (prepared by dissolving 0.5 gram of morphine in an excess of dilute sulphuric acid and diluting to 50 cc.) and a little chloroform. If iodine is present, a violet color will be imparted to the chloroform. To test bromide of potassium for iodine by the same method, the solution of the bromide is first treated with two or three drops of pure bromine water. To determine the halogens in chlorates, bromates and iodates, F. Fleissner[1] boils the solutions containing them for an hour with an excess of zinc dust. The reduction is complete. In the case of chlorates only is it necessary to acidify with acetic acid. Perchlorates are not reduced by this treatment.

Nitrogen.—W. H. Perkin[2] uses a mixture of precipitated manganic oxide and chromate of potassium to remove the oxides of nitrogen formed when nitrogenous organic compounds are burned for the purpose of determining carbon and hydrogen. The mixture fills from four to six inches of that portion of the combustion tube usually occupied by metallic copper, and, if the temperature is kept sufficiently low (200°–250°), will completely absorb and retain any oxides of nitrogen formed. The author recommends, in view of the fact that manganic oxide may contain alkali, the use of a chromate containing about 10 per cent. of bichromate. Mixtures of chromate and oxide in the proportions of 1 : 2 and 2 : 1 were employed in the experiments described. The mixture will also absorb sulphuric and sulphurous acids, but the temperature required is higher than the retention of the nitrogen compounds will admit of. A difficulty which would, therefore, present itself when an organic compound containing both nitrogen and sulphur is burned with oxide of copper might be obviated by using a larger quantity of the mixture and heating to a high temperature that portion only which is nearest to the substance.

New forms or arrangements of apparatus designed to facilitate the collection and measurement of the nitrogen obtained by Dumas' method have been described by H. Schwarz,[3] E. Ludwig,[4] H. Schiff,[5] K. Zulkowsky,[6] C. E. Groves[7] and W. Staedel.[8] In order that the same combustion tube may serve for several determinations, Zulkowsky and Groves place the material from which the carbon dioxide is to be obtained in a separate tube and connect the two by means of a smaller tube. Zulkowsky recommends surrounding the tube, which serves as a carbon-dioxide generator, with a cylinder of sheet iron, which may be shoved backwards or forwards. In this manner the heat is uniformly distributed and a more constant current of gas obtained.

Arsenic.—L. Mayer[9] determines arsenious acid in the presence of arsenic acid by means of its reducing action upon an ammonia-

[1] Monatshefte für Chemie, **1**, 313. [2] Journ. Chem. Society, 1880, 121, 457.
[3] Ber. d. deutsch. chem. Gesell. **13**, 771. [4] Ibid. **13**, 883. [5] Ibid. **13**, 885. [6] Ibid. **13**, 1096.
[7] Journal Chem. Society, **13**, 500. Also Berichte d. deutsch. chem. Gesell. **13**, 1341.
[8] Zeitschrift analyt. Chemie, **19**, 452. [9] Jour. prak. Chemie, **22**, 103.

cal solution of silver nitrate. The reaction which takes place is represented by the following equation: $As_2O_3+2Ag_2O=As_2O_5+4Ag$.

The arsenious acid or mixture of arsenious and arsenic acids is dissolved in ammonia, poured into a strongly ammoniacal solution of nitrate of silver, and the whole boiled about thirty minutes. The metallic silver may be collected, washed with water containing ammonia and chloride of ammonium and weighed as such, or dissolved and precipitated as chloride.

E. Fischer[1] finds it practicable to separate arsenic quantitatively from the other metals precipitated by sulphide of hydrogen by distilling with ferrous chloride and hydrochloric acid. The material containing the arsenic, if an alloy, is dissolved by means of hydrochloric acid and chlorate of potassium; if a mixture of sulphides of arsenic, antimony and tin, it is prepared by treating the alkaline solution with chlorine. The excess of chlorate of potassium is then nearly destroyed by warming for a short time with concentrated hydrochloric acid. If nitric acid has been used it must be removed by evaporating with sulphuric acid. The solution is placed in a globe-shaped flask holding from 500 to 600 cc., treated with 20 cc. of a saturated solution of ferrous chloride and with 20 per cent. hydrochloric acid until the volume equals about 140 cc. The flask is then connected with a cooler, and the contents distilled until the volume of the residue has been diminished to 30 or 35 cc. If the distillation is continued beyond this point other chlorides may volatilize. If the quantity of arsenic to be removed does not exceed 0.01 gram, one distillation suffices. If more is present, hydrochloric acid must be added to the residue and the distillation repeated. The separation of arsenic from lead, copper, bismuth, cadmium and mercury is complete. The distillate may however contain small quantities of the chlorides of tin and antimony, but their presence does not interfere with the volumetric determination of the arsenic. If the distillate is treated with ferrous chloride and redistilled until the residue has been diminished to 30 cc., the arsenic will be completely freed from both tin and antimony.

Carbon.—T. Weyl and B. von Anrep[2] give the following points for the chemical diagnosis of poisoning by carbon monoxide:

1. The blood is to be preserved in fully filled flasks and kept until wanted for examination in a dark and cool place.

2. If, on addition of sulphide of ammonium or the solution of ferrous-ammonium tartrate of Stokes, no reduction to hemoglobine takes place, carbon monoxide-hemoglobine is present.

3. If, on addition of a few drops of an 0.025 per cent. permanganate solution to the diluted blood, no methemoglobine appears within twenty minutes—if the blood remains clear and red, carbon monoxide-hemoglobine is present. The same quantity of permanganate added to an equally dilute solution of human blood or that of the ox, dog or rabbit, should give a yellow color, produce methemoglobine and render the solution turbid.

[1] Berichte d. deutsch. chem. Gesell. **13,** 1778. [2] Ibid. **13,** 1294.

4. Instead of the permanganate, a 1 per cent. solution of pyrocatechine or hydroquinone can be used, but they must be digested with the blood for 15 minutes at a temperature of 40°.

5. The spectra of hematine in acid solution and of methemoglobine can be easily distinguished only by the spectroscopic measurement of the position of the absorption bands.

By agitating 10 cc. of blood from five to seven times with six liter portions of the air to be tested, heating the blood to 90° or 95°, and passing a current of air through it, and then through an aqueous solution of palladium chloride, containing 1 part of the chloride to 50 of water, S. von Foder[1] is able to detect the presence of 0.5 of one volume of carbon monoxide in 10,000 of air. Metallic palladium is precipitated according to the following equation: $PdCl_2 + CO + H_2O = CO_2 + 2HCl + Pd$.

By this method the author detected carbon monoxide in the blood of rabbits which had been kept for some time in an atmosphere containing only 0.4 of 1 part of the gas in the 10,000.

He recommends, also, the use of test papers prepared by moistening fine filter paper with a 0.2 per cent. solution of palladium chloride. A strip of the dried paper is suspended from a platinum wire in a 10 liter flask containing the air to be examined, and a little water. The flask is then closed. If the air contains $\frac{1}{30000}$ of carbonic oxide by volume, the paper becomes covered with a black film within a few minutes; if $\frac{1}{100000}$, after 2 to 4 hours; if $\frac{1}{300000}$, after 12 to 24 hours. It is however to be remembered that sulphide of hydrogen and ammonia will also blacken the papers.

To determine carbon monoxide quantitatively, a large volume of the air is passed through a series of absorption apparatus filled with a neutral solution of palladium chloride, the metallic palladium collected, dissolved in aqua regia, and subsequently determined by means of a standard solution of potassium iodide.

A. W. Hofmann[2] finds that triethylphosphine can be advantageously employed for the quantitative determination of carbon disulphide. A tubulated retort containing the compound is placed upon a water-bath, and connected with a cooler and receiver. The receiver is then connected with a series of three wide test tubes partially filled with caustic soda and a solution of triethylphosphine in ether. A current of dry carbon dioxide is passed through the apparatus and the retort heated. The operation is continued for several hours. The precipitate ($(C_2H_5)_3PCS_2$) is finally collected upon a weighed filter, dried in a vacuum and weighed. The method is especially adapted to the detection and determination of small quantities of carbon disulphide. By means of it the author found this compound in samples of mustard oil whose genuineness could not be questioned.

H. N. MORSE.

[1] Dingler's polytechn. Jour. **237**, 456. [2] Berichte d. deutsch. chem. Gesell. **13**, 1732.

NOTES.

The Density of Iodine Vapor.

Victor Meyer concluded from Troost's experiments that the method of Dumas as well as his own for determining vapor densities gave the same results, and withdrew his suggestions to explain the possibility of disagreement. Crafts and Meier had suggested at the same time as V. Meyer that a diminution of tension due to the presence of air in the dissociable vapors, might cause a difference in the results of the two methods, and to this they still adhere. Troost afterwards established the variation of density with tension, and his conclusion was against the hypothesis of dissociation; to this CRAFTS and MEIER take exception. They have experimented with various methods and express their results graphically in the form of curves. These show that at a low temperature, 355° for example, the density of iodine vapor is normal, and has the same coefficient of expansion and of compressibility as air. For tensions of .1, .2, .3 and .4, the variation of density increases toward the middle of the curves, and becomes zero at high temperatures. Thus with low tensions also the density becomes constant between 1400° and 1520°, and equal to one-half the original. All facts accord with the hypothesis of gradual dissociation of the molecule I_2. This cannot be proved as in Deville's classical work, since the substance remains homogeneous; but the phenomena are such as would be observed if there were such dissociation, and this hypothesis offers the only explanation of the limit of diminution at one-half. The tendency of diminished tension to increase dissociation is well known.

The authors express the hope of being able to furnish a numerical basis for the speculation in the decomposition of the so-called elements founded on spectroscopic observations.—(*Comptes rendus*, *Jan.* 3, 1881.)

On Ozone.

HAUTEFEUILLE and CHAPPUIS have further studied, by means of the spectroscope, the formation and destruction of ozone with the following results: The absorption bands of ozone pure and dry, and formed from oxygen free from nitrogen, disappear slowly at ordinary temperatures, rapidly at red heat; and this takes place whether the ozone is enclosed in a vessel or is in the form of a gaseous current, the spectrum finally becoming continuous without the appearance of any new lines. The same phenomenon is observed in the destruction by heat of ozone mixed with nitrogen, the latter not having been exposed to electrical influence. There

is no indication of the formation of hyponitric acid. It is admitted that in ozonising oxygen in the presence of nitrogen at low electrical tensions, no hyponitric acid is formed. But the authors find that in ozonising at ordinary temperatures a mixture containing one-seventh nitrogen, there is always produced a new substance, indicated by remarkable absorption bands differing from those of electrified nitrogen, of nitrous, hyponitric and nitric acids. If the gas be passed through water the latter becomes acid, and the gas shows the spectrum of ozone only. So, too, if the gas be not dry, the new lines rapidly disappear. The same gaseous mixture is quickly destroyed at red heat, the bands of ozone and of the new substance disappearing, and those of hyponitric acid appearing and persisting. If the slow decomposition at ordinary temperatures be followed with the spectroscope, it is seen that the new bands disappear in from 24 to 48 hours before there is a trace of hyponitric acid. The latter then slowly appears; from which the authors conclude that the new substance decomposes into oxygen and nitric anhydride, and the latter into oxygen and hyponitric acid. Berthelot had observed that a mixture of hyponitric acid and oxygen subjected to electrical influence became colorless, and the authors in repeating the experiment find in the resulting mixture the new substance, but no hyponitric acid. They suggest the probable existence of a pernitric acid analogous to the persulphuric acid discovered by Berthelot.—(*Comptes rendus, Jan.* 10, 1881.)

On Nitrification.

Schönbein attributed the formation of nitrates to the union of ozone and nitrogen, but Berthelot has stated that this union does not take place directly. HAUTEFEUILLE and CHAPPUIS have shown, however, that it does take place under the influence of electricity of low tension with the production of a new substance, probably pernitric acid. The gaseous mixture was subjected to the influence of electricity of very low tension. The ozone was so diluted that it did not show absorption bands in a column two meters long, but there was a suspicion of bands of pernitric acid. When the current was heated with an alcohol lamp these appeared distinctly. The electrical tension was then increased as much as the apparatus would allow. The amount of pernitric acid formed increased progressively, but no hyponitric acid was obtained directly. The authors suppose that the formation of hyponitric acid, even at high tensions, may be due to the decomposition of pernitric acid by the greater heat of discharge.

Studying the effect of heat alone upon pernitric acid, they find that it is decomposed at all temperatures, but that at 130° the decomposition is completed in a few seconds, yielding oxygen and hyponitric acid. In order that the formation of pernitric acid should take place in the atmosphere, the presence of water vapor must be

no obstacle. The authors found, however, that the absorption bands of pernitric acid did not appear if the gas was not perfectly dry, but in this case liquid acid condensed upon the walls of the containing vessel. Thus by passing three liters of air with water vapor through the apparatus, they obtained .054 gram of nitric acid. From these experiments it is seen that nitric acid may be formed under varying conditions by the union of oxygen, or ozone, and nitrogen under the influence of electricity of low tension, pernitric and hyponitric acids being intermediate products.—(*Comptes rendus, Jan.* 17, 1881.)

Picene.

C. GRAEBE and J. WALTER have investigated more fully a hydrocarbon first obtained by O. Burg from the tar of brown coal, and called by him picene. The same compound is readily obtained when the residue from the rectification of California petroleum is subjected to dry distillation at a red heat. It is crystalline, and fuses at about 250°. It possesses a greenish yellow color, the lamellæ being often intensely green, the powder more yellowish. According to the analyses the substance has the formula $C_{21}H_{14}$ or $C_{22}H_{14}$. In perfectly pure condition it is colorless, and fuses at 330°–335°. It is possible that the crude material with which the authors worked is identical with which Morton worked some years ago. The hydrocarbon isolated by Morton and called thallene by him, is probably not quite pure picene, though from the published accounts of thallene it is impossible to decide this point. The boiling point of the substance was determined by the aid of the air thermometer constructed by Crafts, and was found to be 518–520°.—(*Ber. d. deutsch. chem. Gesell.* 14, 175.)

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